Models of electromagnetic properties of composite media

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Models of electromagnetic properties of composite media

by

Jin Liu

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University
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2012

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Electromagnetic composite materials have attracted much interest in recent years, due to their desirable microwave and optical applications. One class of these is negative refractive index materials, or double negative materials, in which both permittivity and permeability of materials are simultaneously negative. Many exciting potential applications of double negative materials have been proposed, such as the perfect lens and the cloaking device. Here, a simple-cubic lattice of identical, homogeneous or coated non-metallic spherical particles embedded in a matrix is analyzed. One contribution of this work is the derivation of an analytical formula for the threshold dielectric loss angle of spherical inclusions, above which DNG behavior of the system is extinguished. In addition, analytical formulas are derived from which double negative bandwidth of a simple-cubic lattice of identical, magnetodielectric homogeneous or coated spheres can be determined.

Another case of interest is nanocomposites, which commonly consist of nanoparticles embedded in a polymer matrix. These materials show superior dielectric or mechanical performance by taking advantage of the merits of their individual non-hybrid components. In one manifestation, diblock copolymers can be utilized to spatially separate nanoparticles by incorporating them in one block, preferentially, to form a long-range ordered structure. By designing this structure, the electromagnetic properties can be tailored for potential applications in novel devices. Here, molecular dynamics of polymer matrices and nanocomposites is analyzed by parametric modeling of their dielectric spectra, supporting design of a composite with desired electromagnetic properties.
Firstly, I would like to express my deepest gratitude to my advisor Dr. Nicola Bowler for her inspirational guidance, support and encouragement throughout my graduate study. Thanks to my previous and current committee members for being my committee members and providing valuable guidance.

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CHAPTER 1. Introduction

Composite materials consist, generally speaking, of two or more constituent materials with different physical or chemical properties and may naturally exist or be artificially engineered to exhibit excellent mechanical or dielectric properties which are generally superior to those of their individual components. Practical applications of composites can be seen almost everywhere in daily life, such as in the use of steels, fiberglass and concrete. The usefulness of composites lies in their ability to combine the advantages of the non-hybrid components. For example, reinforced concrete, which consists of concrete and steel, is light and strong, whereas concrete alone is light but fragile while steel itself is strong but heavy. Although composite materials show discontinuity in material properties on a length scale that is similar to that of their phases, on a much larger scale they behave like a homogeneous medium in their electromagnetic or mechanical properties, for example. Homogenization of composite materials provides a convenient and effective way to describe their physical properties by regarding composites as an effective homogenous medium, and many classic mixing formulas, such as the Maxwell-Garnett [1] and Bruggeman [2] mixing formulas, may be employed to describe their effective physical properties by using physical parameters of the constituent materials and their volume fractions, and theoretical results predicted by these classic formulas agree with some experimental data quite well.

1.1 Metamaterials

Metamaterials form one class of electromagnetic composites that are artificially fabricated to exhibit extraordinary electromagnetic properties. Due to their desirable microwave and optical applications, metamaterials have attracted much interest in recent years [3].
One example is that of negative refractive index materials, also called left-handed or double negative (DNG) materials, in which both the permittivity and permeability of the structure are negative simultaneously. These were studied theoretically by Veselago [4]. Thirty years later, the first negative refractive composite materials made of split ring resonators and a metallic array were fabricated and verified experimentally [5]. A lot of exciting potential applications have been proposed, such as the perfect lens predicted by Pendry [6], and the cloaking device, demonstrated at microwave frequencies in 2006 [7]. Nevertheless, periodic split ring resonators are anisotropic structures and exhibit losses that become more significant as the frequency of operation increases, due to metallic components. Following the theoretical work developed by Lewin in 1947 [8], it was theoretically shown by Holloway et al in 2003 that a composite medium consisting of non-metallic, magneto-dielectric spherical particles embedded in a matrix can exhibit DNG behavior for wavelengths where Mie resonance occurs in the spherical inclusions [9].

The contribution of this work in the area of double negative materials lies in the study of i) a simple cubic system of identical homogeneous spheres and ii) coated spheres, embedded in a matrix. The effect of losses of spherical inclusions on DNG behavior of a simple-cubic composite system is analyzed in Chapter 2. An analytical expression for the threshold dielectric loss angle of spherical inclusions, above which DNG behavior is extinguished, is derived by using the Möbius transformation and the dipole approximation of Mie’s theory of scattering by a sphere [10]. The formula can provide an estimate of acceptable particle losses for practical design of DNG materials. In Chapter 3, the percentage bandwidth in which permittivity and permeability of a simple-cubic lattice of identical, magnetodielectric spheres are simultaneously negative, is analyzed based on Mie scattering theory [10] and effective medium theory. By employing a modified form of Lewin’s formulas [8], a contour of DNG bandwidth of all possible values of permittivity and permeability is given as a practical guide to design DNG materials with optimized DNG bandwidth. In Chapter 4, an explicit analytic expression for the effective permittivity or permeability of a simple-cubic array of coated spheres in a matrix is derived by the method of Hertz potential expansions under the effective medium regime and the dipole
approximation. In this system, a dielectric spherical core gives rise to negative permeability due to Mie resonances and a semiconductive shell gives rise to negative permittivity for frequencies below its plasma frequency. By modeling, the spheres may be designed so that the regions of negative permeability and permittivity overlap, giving rise to DNG behavior. A contour map of double-negative (DNG) bandwidth as a function of particle radius and core/shell radius ratio is plotted for one example system consisting of LiTaO$_3$/Si particles embedded in a polystyrene foam matrix for volume fraction $f = 0.5$. From the contour map, the case that exhibits the largest possible DNG bandwidth can be easily identified.

1.2 Nanocomposites

Another important engineering example of composite materials are nanocomposites, which commonly consist of nanoparticles embedded in a polymer matrix. These materials show superior dielectric or mechanical performance by taking advantage of the merits of their individual non-hybrid components. In one manifestation, diblock copolymers can be utilized to spatially separate nanoparticles by incorporating them in one block, preferentially, to form a long-range ordered structure. By designing this structure, the electromagnetic properties can be tailored for potential applications in novel devices. The self-assembly behavior of block copolymers into long-range order morphologies has been investigated for several decades. Depending on the molecular weights of the blocks and on the polymerization process, the linear diblock copolymer can be phase-separated to form different morphologies, such as spherical, lamellar, cylindrical and inter-connected structures.

The block copolymer PS-$b$-PMMA, consisting of PS and PMMA blocks covalently connected at one end, is widely used as a polymer matrix for nanocomposites. In Chapter 5, the dielectric relaxation properties of poly(methyl methacrylate) (PMMA) and polystyrene-$b$-poly-(methyl methacrylate) (PS-$b$-PMMA) diblock copolymers are investigated by broadband dielectric spectroscopy and parametric fitting techniques based on the Havriliak-Negami model [13]. The contribution of this work lies in the examination of the molecular dynamics of this block copolymer for two molecular weights of PMMA and in comparison with the molecular
dynamics of a simple blend, revealed by dielectric spectroscopy.

Segmented polyurethanes, studied in Chapter 6, are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. At low temperatures, these materials exhibit the properties of cross-linked elastomers, which exhibit hydrogen bonded cross-linking phase-separated urethane blocks. This phase separation gives rise to hard ‘glassy’ domains dispersed in a soft ‘rubbery’ matrix, leading to the elastomeric properties of segmented polyurethanes. Because polar groups exist in both the soft and hard segments of segmented polyurethanes, dielectric spectroscopy is a natural and effective method to investigate their relaxation behaviors, which are associated with their molecular dynamics. In Chapter 6, EN8 segmented polyurethanes are studied by the method of broadband dielectric spectroscopy and parametric fitting techniques to investigate the effect of the n-hexylcarborane content on observed reinforcement of the hard PU segments and plasticization of the soft PBD segments. Because of their highly stable, non-toxic and chemically modifiable properties, boron cage compounds are used as nano-fillers to improve the neutron absorbing/shielding property of the composite.

References


CHAPTER 2. Analysis of Losses in a Double-Negative (DNG) Metamaterial Composed of Magnetodielectric Spheres Embedded in a Matrix

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Jin Liu, Nicola Bowler

A simple-cubic lattice of identical, magnetodielectric spheres exhibiting double-negative (DNG) behavior is analyzed. An analytic expression for the threshold loss angle $\delta_{th}$ of the spheres, above which DNG behavior is extinguished, is derived by utilizing the Möbius transformation. The formula is valid for either dielectric or magnetic loss exhibited by the particles, and is derived based on the dipole approximation of Mie’s theory of scattering by a sphere. For spheres with equal real relative permittivity and permeability, it is shown that $\delta_{th}$ increases as particle volume fraction increases. It is also shown that the loss angle of the effective medium can be controlled by appropriate choice of frequency.

Composite metamaterial, negative refractive index, spherical inclusions, losses, Mie theory, Möbius transform.

2.1 Introduction

A simple-cubic lattice of identical, magnetodielectric spheres exhibiting double-negative (DNG) behavior is analyzed. An analytic expression for the threshold loss angle $\delta_{th}$ of the spheres, above which DNG behavior is extinguished, is derived by utilizing the Möbius transformation. The formula is valid for either dielectric or magnetic loss exhibited by the particles, and is derived based on the dipole approximation of Mie’s theory of scattering by a sphere. For
spheres with equal real relative permittivity and permeability, it is shown that $\delta_{th}$ increases as particle volume fraction increases. It is also shown that the loss angle of the effective medium can be controlled by appropriate choice of frequency.

### 2.2 Derivation of Analytic Expression for the Threshold Loss Angle $\delta_{th}$

Double-negative (DNG) metamaterials, which are also termed “left-handed” or “negative-index” materials, offer some intriguing physical properties [1] with interesting potential applications in the fields of optical and microwave technology. One example application is the perfect lens predicted by Pendry [2] in which not only are the propagating components of the electromagnetic wave brought to a focus by a planar DNG slab with refractive index equal and opposite to that of the environment, but so are the evanescent components that are lost to damping in a conventional optical lens. Another example is the cloaking device, demonstrated at microwave frequencies in 2006 [3]. The development of DNG metamaterials for microwave transmission line applications is also an active area of research [4].

A DNG is so-called because both the real parts of the over-all permittivity and permeability of the medium are negative simultaneously. This leads to propagation of a “backward wave” in which the phase velocity and group velocity of the wave have opposite signs. In other words, the direction of the phase velocity is opposite to that of the energy flow.

Despite the predicted advantages of the perfect lens over the classical optical lens, it has been pointed out that practical limitations still exist on the resolution of a lens that is designed to be perfect, according to the definition above, due to the inherent periodicity of the metamaterials that may be used to construct it and due to losses that exist in all real materials [5]. An approximate analytic expression is given in [5] for the resolution enhancement of the perfect lens, as compared with the limit of optical resolution, for small deviations in either the real or imaginary parts of the lens permittivity and permeability from the ideal values ($-1$).

Here, an analytic expression for the threshold loss angle of the spheres’ permittivity or permeability, $\delta_{th}$, above which DNG behavior is extinguished, is given for a simple-cubic array of magnetodielectric spheres in terms of the electromagnetic parameters of the constituents.
and the volume fraction of the spheres.

Define the loss angle $\delta_i$, $i = \varepsilon, \mu$ as

$$\tan \delta_\varepsilon = \varepsilon''/\varepsilon'$$

and

$$\tan \delta_\mu = \mu''/\mu'$$

(2.1)

wherein permittivity and permeability are, respectively, $\varepsilon = \varepsilon_0(\varepsilon_r' - j\varepsilon_r'')$ and $\mu = \mu_0(\mu_r' - j\mu_r'')$.

These forms arise from the assumption that the time-dependence of the electromagnetic wave is as $\text{Re}[\exp(j\omega t)]$. The subscripts ‘0’ and ‘r’ denote free-space and relative values, respectively.

DNG behavior pertains for $\varepsilon_r' < 0$ and $\mu_r' < 0$.

In many realizations of DNG materials, $\varepsilon_r' < 0$ is provided by a metallic element near the plasma frequency, and $\mu_r' < 0$ by a split-ring resonator, also metallic. These elements are arranged periodically, resulting in a highly anisotropic material that exhibits DNG behavior for electromagnetic radiation that is incident on it over a narrow range of angles. The utilization of metallic elements makes the resulting metamaterial highly lossy, leading to complications in some practical applications [6]. On the other hand, it was shown theoretically by Holloway et al in 2003 that a composite medium consisting of non-metallic, magnetodielectric spherical particles embedded in a matrix can exhibit DNG behavior for wavelengths where resonances are excited [7]. More recently it has been shown that isotropic DNG metamaterials cannot be formed from arrays of identical purely dielectric spheres [8]. The work of Holloway et al was based on theory developed by Lewin [9], in which a low-order solution according to Mie scattering theory is obtained for a plane wave incident on a simple-cubic array of magnetodielectric spheres. Mie resonances provide both $\varepsilon_r' < 0$ and $\mu_r' < 0$ over certain frequency bands, which are typically narrower than those achievable using metallic elements. In an array of magnetodielectric spheres, the effect of loss is to dampen the desired resonances that yield DNG behavior. Holloway et al discussed the fact that all realistic materials exhibit some loss, but did not obtain an analytical expression for the threshold value of loss in terms of values of the constituent material parameters and particle volume fraction.

For an array of homogeneous spheres with relative permittivity $\varepsilon_r2$ and permeability $\mu_r2$ arranged on the nodes of a simple-cubic lattice and embedded in a matrix with relative permittivity $\varepsilon_r1$ and permeability $\mu_r1$, the relative effective permittivity $\varepsilon_{re}$ and permeability $\mu_{re}$ of
the mixture are given by expressions that are formally similar to the Maxwell-Garnett mixture formula [7], [9]:

\[
\varepsilon_{re} = \varepsilon_{r1} \left( 1 + \frac{3f}{\varepsilon_{rp} + 2\varepsilon_{r1} - f} \right).
\]  
(2.2)

For brevity, the analysis here will be conducted in terms of permittivity, but equivalent equations hold for permeability. In the quasi-static regime, \(\varepsilon_{rp}\) is none other than \(\varepsilon_{r2}\) and equation (4.35) reduces to the true Maxwell-Garnett formula. In the case in which the wavelength within the particle, \(\lambda_2\), is similar to the particle diameter \(2a\), however, the effective permittivity of the particles \(\varepsilon_{rp}\) is given by [7], [9]

\[
\varepsilon_{rp} = F(\theta)\varepsilon_{r2}.
\]  
(2.3)

The function \(F(\theta)\) that represents the coupling of the electric and magnetic fields is given by

\[
F(\theta) = \frac{2(\sin \theta - \theta \cos \theta)}{(\theta^2 - 1)\sin \theta + \theta \cos \theta},
\]  
(2.4)

where \(\theta = k_0a\sqrt{\varepsilon_{r2}\mu_{r2}}\), \(k_0 = 2\pi/\lambda_0\) is the wave number in free space and \(\lambda_0\) is the wavelength in free space. Mie resonances appear through the form of \(F(\theta)\), Eq. (3.4). In order to determine the threshold loss angle \(\delta_{th}\), an expression for the loss angle of the particle, \(\delta_{\varepsilon}\), is sought in terms of the other parameters of the system and then the condition \(\varepsilon'_{re} = 0\) is imposed. Writing \(\varepsilon^*_{ri} = \varepsilon_{ri}/\varepsilon_{r1}, i = 2, e\), Eq. (4.35) can be rearranged to give

\[
\varepsilon^*_{re} = \frac{\varepsilon^*_{r2}(1 + 2f)F(\theta) + 2(1 - f)}{\varepsilon^*_{r2}(1 - f)F(\theta) + (2 + f)},
\]  
(2.5)

which is the standard form of the Möbius transformation [10]:

\[
T(z) = \frac{az + b}{cz + d}, \quad \text{where} \quad ac - bd \neq 0.
\]  
(2.6)

In Eq. (2.5), therefore, \(\varepsilon^*_{re}\) can be treated as the Möbius transformation of \(F(\theta)\), which can be written as

\[
\varepsilon^*_{re} = T[F(\theta)].
\]  
(2.7)

A complex-plane plot of \(F(\theta)\) for a range of frequencies either side of the first Mie resonance is given in Fig. 2.1, for \(\delta_{\varepsilon} = 0.1\). A corresponding Cole-Cole plot of \(\varepsilon^*_{re}\) is shown in Fig. 2.2.

The plots of Figs. 2.1 and 2.2 are related by the transformation (2.7). When \(\delta_{\varepsilon} = 0\), \(F(\theta)\)
Figure 2.1: Complex plane plot of $F(\theta)$, Eq. (3.4), for $\varepsilon_{r2}^{*} = 2$, $\delta_\varepsilon = 0.1$ and $f = 0.3$.

Figure 2.2: Cole-Cole plot of $\varepsilon_{r}\varepsilon^*$, Eq. (4.35), with parameters as given for Fig. 2.1.
runs from $1 \to \infty$ and $-\infty \to 0$ on the real axis in Fig. 2.1. The low frequency limiting value of $F(\theta)$ occurs at unity, denoted $x_1$ in the figure. Similarly, $\varepsilon_r^*$ is also real when $\delta_\varepsilon = 0$, and the low-frequency limiting value is denoted $x_1'$. When $\varepsilon_r^*$ is lossy, the locus of points in the complex-plane describe counter-clockwise spirals that decay gently as frequency increases. The rate of decay increases as $\delta_\varepsilon$ increases. Note that the loss angle of variable $\theta$ is $\delta_\varepsilon/2$, because $\theta \propto \sqrt{\varepsilon_r^2}$. There exists only one curve in correspondence with a particular value of the loss angle $\delta_\varepsilon$ in each of the complex planes of $F(\theta)$ and $\varepsilon_r^*$. This means that if the features of the plot of $F(\theta)$ are known, then the features of $\varepsilon_r^*$ can be deduced from those of $F(\theta)$. In particular, the straight line $x_s x_1$ is transformed to the straight line $x'_s x'_1$. This fact shall be utilized to derive the analytic expression for $\delta_{th}$ that is sought.

Note that vertical lines drawn from the maxima in Im[$F(\theta)$] and $\varepsilon_r^{**}$, marked $L_s$ and $L'_s$ in Figs. 2.1 and 2.2 respectively, are offset from the $y$-axes shown in the figures, cutting the $x$-axes at $x_s$ and $x'_s$ respectively. Hence, negative $\varepsilon_r^{**}$ is lost, i.e. $\varepsilon_r^{**} > 0$, for $\delta_\varepsilon$ sufficiently large that the entire curve of $\varepsilon_r^*$ plotted as in Fig. 2.2 occurs to the right of the $y$-axis. The condition for threshold loss is that the curve grazes the $y$-axis. Having recognized these points, the properties of the Möbius transform and trigonometry provide an expression for $\delta_{th}$ in terms of the parameters of the system.

Despite the fact that the curves shown in Figs. 2.1 and 2.2 are spirals of decreasing amplitude, it shall be assumed here that they are circular arcs, at least from their starting points denoted $x_1$ and $x'_1$ to the leftmost points on the curves in those figures. This is a reasonable assumption when $\delta_\varepsilon$ is small. The angle between the tangent at the starting point $x_1 = 1$ in Fig. 2.1 and the real axis is $\delta_\varepsilon$, which is approximately the same as the angle between the line $L_s$ and the radial line $Ox_1$. The radius of the arc, $r$, and the loss angle, $\delta_\varepsilon$, are hence related by

$$
\tan \delta_\varepsilon \approx (x_1 - x_s)/r.
$$

The maxima of Im[$F(\theta)$] are located on the line $L_s$ for all values of $\delta_\varepsilon$, and hence the maxima of $\varepsilon_r^{**}$ are also located on the line $L'_s$, due to the fact that the value of $\delta_\varepsilon$ does not influence the frequency, or electrical radius $k_0a$, at which resonance occurs. This means that $x_1 - x_s$
is constant and can be derived by considering $F(\theta)$ for any one value of $\delta_e$. It is found that $x_1 - x_s \approx 0.185$ and, because $x_1 = 1$, $x_s \approx 0.815$.

In terms of the parameters labeled in Fig. 2.2 and by considering the properties of the Möbius transform, it is found that

$$\tan \delta_e \approx (x_1' - x_s')/r' \tag{2.9}$$

When the loss tangent is at its threshold value, the $y$-axis is tangent to the curve depicting $\varepsilon_{\Re}^\ast$ in the complex plane. Under these circumstances the threshold value of $r'$, denoted $r_{th}'$, is given by

$$r_{th}' = x_s' = T(x_s), \quad \text{for} \quad \delta_e = \delta_{th}. \tag{2.10}$$

Applying the Möbius transform to terms on the right-hand-side of Eq. (2.9) finally gives

$$\tan \delta_{th} \approx \frac{T(x_1) - T(2x_s - 1)}{T(x_s)}. \tag{2.11}$$

Note that the arguments of the transformations in Eq. (2.11) are fixed constants whereas the transformation itself is a function of $f$ and $\varepsilon_{\Re}^\ast$, Eqs. (2.5) and (2.6).

To test analytic formula Eq. (2.11), a calculation is made with the parameters considered by Holloway et al., Fig. 8 in Ref. [7], where $\varepsilon_{\Re}^\ast = \mu_{\Re}^\ast = 50$ and $f = 0.5$. (Despite the fact that this analysis under the dipole approximation is applicable for $f \leq 0.3$, this example is chosen in order to compare with an independent result.) Substituting these values into Eq. (2.11) gives $\tan \delta_{th} = 0.046$. In Fig. 2.3 it is shown that the corresponding curve of $\varepsilon_{\Re}^\ast$ grazes the $x$-axis, as it should. This result is supported by those presented in Fig. 8 of Ref. [7], from which it can be deduced that $\delta_{th}$ is slightly greater than 0.04. Other curves shown in Fig. 2.3 (for $\tan \delta = 0$ and 0.2) are identical with those shown in Fig. 8 of Ref. [7].

Further, the way in which $\delta_{th}$ depends on the permittivity or permeability of the particles, $\varepsilon_{\Re}^\ast = \mu_{\Re}^\ast$, is shown in Fig. 2.4. The threshold loss angle $\delta_{th}$ should be regarded as that of either permittivity or permeability so that if $\delta_{th}$ is the dielectric loss angle then the permeability is lossless, and vice-versa. Excluded values of $\varepsilon_{\Re}^\ast$ or $\mu_{\Re}^\ast$ lie in the range $[2, \sqrt{2}]$ for $f \in [0, 1]$, according to the restriction on Eq. (2.6). For this reason the curves in Fig. 2.4 are plotted for $\varepsilon_{\Re}^\ast = \mu_{\Re}^\ast > 2$. It can be seen that, over the considered range of $\varepsilon_{\Re}^\ast = \mu_{\Re}^\ast$, $\delta_{th}$ decreases
Figure 2.3: The real part of the permittivity of the mixture, $\varepsilon_{re}'$, with volume fraction $f = 0.5$ and $\varepsilon_{r2}' = \mu_{r2}' = 50$, for various values of dielectric loss tangent.

Figure 2.4: The threshold loss angle $\delta_{th}$ of the particle versus $\varepsilon_{r2}' = \mu_{r2}'$ for mixtures with volume fractions $f = 0.3, 0.2$ and 0.1.
as $\varepsilon''_{r2} = \mu''_{r2}$ increases. On the other hand, $\delta_{th}$ increases significantly as the volume fraction $f$ increases, pointing towards better success in achieving DNG behavior in practical systems with higher fill factor.

Considering the Cole-Cole plot of $\varepsilon''_{re}$ shown in Fig. 2.2, it can be deduced that for a system composed of lossy dielectric particles (with $\delta_{\varepsilon} < \delta_{th}$ so that DNG behavior pertains) dispersed in a matrix, there is a band of frequencies in the vicinity of point $x'_{s}$ for which the loss angle of the effective medium, $\delta_{\varepsilon}$, is small. In principle, then, appropriate choice of frequency band also permits control of $\delta_{\varepsilon}$. 
References


CHAPTER 3. Analysis of Double-Negative (DNG) Bandwidth for a Metamaterial Composed of Magnetodielectric Spheres Embedded in a Matrix

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Based on Mie scattering theory and effective medium theory, the percentage bandwidth in which permittivity and permeability of a simple cubic lattice of identical, non-metallic magneto-dielectric spheres are simultaneously negative (double-negative or DNG) is analyzed. Relaxing the restriction of previous work, that $k_1a \to 0$ where $k_1$ is the wave number in the matrix and $a$ is the particle radius, new analytical formulas are obtained for $k_1a < \pi/10$, from which the DNG bandwidth can be easily computed. As an example, a contour map of DNG bandwidth for a wide range of values of particle permittivity and permeability is plotted for particle volume fraction $f = 0.3$. From the analytical formulas, it is shown that the maximum achievable DNG bandwidth for a simple cubic lattice of spheres with particle volume fraction $f = 0.3$ is 7.4%, when the particle permittivity and permeability are both approximately 14 times greater than those of the matrix.

Composite metamaterial, negative refractive index, spherical inclusions, bandwidth, Mie theory.

3.1 Introduction

Research in the field of double-negative (DNG) materials, which are also called “left-handed” or “negative-index” materials, has developed very rapidly because of the desirable
optical and microwave properties of these materials. One example application is the perfect lens predicted by Pendry [1]. Another is the cloaking device [2], [3]. The development of DNG materials for microwave transmission line applications is also an active area of research [4], [5].

A DNG is so-called because both the real part of the over-all effective permittivity, $\varepsilon'_{re}$, and the real part of the magnetic permeability, $\mu'_{re}$, are negative simultaneously. This leads to propagation of a "backward wave" in which the phase velocity and group velocity of the wave have opposite signs. In other words, the direction of the phase velocity is opposite to that of the energy flow. Adopting the notation

$$\varepsilon = \varepsilon_0(\varepsilon'_r - j\varepsilon''_r) \quad \text{and} \quad \mu = \mu_0(\mu'_r - j\mu''_r),$$

which follows from the assumption that the time-dependence of the electromagnetic wave is of the form $\Re\{\exp(j\omega t)\}$, DNG behavior clearly pertains for $\varepsilon'_r < 0$ and $\mu'_r < 0$.

In present realizations of DNG materials, $\varepsilon'_r < 0$ is commonly provided by a metallic element near the plasma frequency, and $\mu'_r < 0$ by a split-ring resonator [6]. These elements are arranged periodically, resulting in a highly anisotropic material that exhibits DNG behavior for electromagnetic radiation that is incident on it over a narrow range of angles. On the other hand, it was shown theoretically by Holloway et al that a composite medium consisting of non-metallic, magneto-dielectric spherical particles embedded in a matrix can exhibit DNG behavior for wavelengths where resonance occurs [7]. The work of Holloway et al is based on theory developed by Lewin [8], in which a low-order solution according to Mie scattering theory is obtained for a plane wave incident on a simple cubic array of magneto-dielectric spheres. It is worth noting that, although the theoretical development relies on the simple cubic lattice arrangement of particles, the dipolar treatment of the particle polarizations is independent of microstructure and so is in principle valid for a random dispersion of spheres in a matrix, provided that the particles are well-separated.

In related work, Vendik et al [9] proposed a metamaterial in which spherical dielectric inclusions are of two different radii, rather than identical and magneto-dielectric as studied here. Two sub-lattices of inclusions with different radii were employed so that the resonances in $\varepsilon$ and $\mu$ can be individually tuned in order to coincide. Ahmadi and Mosellaei [10] consider
spherical and cylindrical inclusions with a full-wave finite-difference time-domain treatment giving visualization of the electric and magnetic field distributions for resonant dipolar and higher-order modes. In an approach that is complementary to that of Vendik et al [9], DNG behavior is designed in [10] by the use of inclusions of the same size but with two distinct permittivity values. The overlap of negative $\varepsilon$ and $\mu$ is controlled by selection of the two permittivity values of the inclusions. Combining the approaches of [9] and [10] raises the possibility of using a variety of particle sizes and permittivity values in the design of a DNG metamaterial. Indeed, the recent analysis of Shore and Yaghjian [11], [12], in which exact solutions for dispersion relations of electromagnetic waves propagating on a simple cubic lattice of magnetodielectric spheres are obtained, can deal with this more arbitrary case.

Analysis presented here is based on the theoretical framework adopted in the work of Holloway et al [7], i.e. a low-order solution of Mie scattering theory for a plane wave incident on a simple cubic array of spherical particles is considered. This approach has the advantage of simplicity, subject to certain restrictions. A new analytical formula valid for $k_1a < \pi/10$, where $k_1$ is the matrix wavenumber and $a$ the particle radius, is presented. This means that the restriction $k_1a \rightarrow 0$ enforced in [7] and [8] is loosened and the results are more widely applicable. As an example, a contour map of DNG bandwidth for a wide range of values of particle permittivity and permeability is plotted for particle volume fraction $f = 0.3$. From the analytical formulas, it is shown that the maximum achievable DNG bandwidth for a simple cubic lattice of spheres with particle volume fraction $f = 0.3$ is 7.4%, when the particle permittivity and permeability are both approximately 14 times greater than those of the matrix.

### 3.2 Theory

To investigate the electromagnetic response of a system of particles embedded in a host medium, it is common to employ an effective medium approach in which the wavelength of the incident field in the mixture is assumed to be significantly greater than the dimension of the particles. If the wavelength within the particles is also long, then the response is quasi-static.
and the electric and magnetic fields are decoupled. The effective permittivity and permeability of the mixture may each be described by the Maxwell-Garnett formula, for example. If, on the other hand, the wavelength within the particles is similar to the particle diameter then the dynamic Maxwell equations apply, within the particle, and the electric and magnetic fields are coupled. This is the problem solved by Lewin [8] for a simple cubic array of spheres embedded in a host medium. In Lewin’s treatment, the particle size is assumed sufficiently small that only the first term in an infinite series of vector wave functions representing the plane wave scattered by a sphere is needed. This puts a restriction on the relative dimensions of the wavelength of the incident wave in the matrix material and the particle radius. In addition, the particle volume fraction is assumed sufficiently small that interparticle interactions are not important and electric and magnetic polarizations in response to the applied field can be regarded as dipolar.

3.2.1 Approximation $k_1a \to 0$

Here $k_1$ refers to the wave number in the matrix and $a$ is the particle radius. For an array of homogeneous spheres arranged on the nodes of a simple cubic lattice and embedded in a matrix with relative permittivity $\varepsilon_{r1}$ and permeability $\mu_{r1}$, Fig. 3.1, the relative effective permittivity $\varepsilon_{re}$ and permeability $\mu_{re}$ of the mixture are given by expressions that are formally similar to the Maxwell-Garnett mixture formula [7]

\[
\varepsilon_{re} = \varepsilon_{r1} \left( 1 + \frac{3f}{\frac{\varepsilon_{r1} + 2f\varepsilon_{rp}}{\varepsilon_{rp} - \varepsilon_{r1}} - f} \right),
\]  

(3.2)

where $f$ is the volume fraction of the spherical inclusions. For brevity, this analysis is conducted in terms of permittivity; equivalent equations hold for permeability. In the quasi-static regime, $\varepsilon_{rp}$ is simply $\varepsilon_{r2}$ and (4.35) reduces to the Maxwell-Garnett formula. In the case in which the wavelength within the particle, $\lambda_2$, is similar to the particle diameter $2a$, however, the effective permittivity of the particles $\varepsilon_{rp}$ is given by $[7][9]$

\[
\varepsilon_{rp} = F(\theta)\varepsilon_{r2}.
\]  

(3.3)
The function $F(\theta)$ that represents the coupling of the electric and magnetic fields is given by

$$F(\theta) = \frac{2(\sin \theta - \theta \cos \theta)}{(\theta^2 - 1) \sin \theta + \theta \cos \theta} \quad k_1 a \to 0 \quad (3.4)$$

where $\theta = k_0 a \sqrt{\varepsilon'_{r2} \mu'_{r2}}$, $k_0 = 2\pi/\lambda_0$ is the wave number in free space and $\lambda_0$ is the wavelength in free space. The possibility of resonant behavior arises through the form of $F(\theta)$ which represents the coupling between the electric and magnetic fields in the system.

Considering (4.35) it can be seen that $\varepsilon_{re}$ is at resonance when the effective permittivity of the particle is negative

$$\varepsilon_{res} = -\varepsilon_{r1} [(2 + f)/(1 - f)] \quad (3.5)$$

From (3.3) and by consideration of the behavior of $F(\theta)$ it is possible to determine how to engineer $\varepsilon_{rp}$ to achieve resonance and, therefore, negative bulk permittivity of the composite; $\varepsilon'_{re} < 0$ for a band of frequencies just above the resonance frequency. Mie theory describes the interaction of a plane wave with a dielectric sphere [13]. The solution is obtained by expanding all fields in spherical vector wavefunctions (eigenmodes) and, in resonance, one eigenmode of the sphere is strongly excited. Each eigenmode displays an infinite number of resonances as a function of the size parameter of the sphere (here $\theta = k_0 a \sqrt{\varepsilon'_{r2} \mu'_{r2}}$), so that even with low-order Mie scattering theory multiple resonances are predicted.

Proceed by making the approximation $\theta^2 \gg 1$ so that $\theta^2 - 1 \approx \theta^2$. Rewriting the right-hand-side of equation (3.4) gives an approximate simplification for $F(\theta)$, written $\tilde{F}(\theta)$

$$\tilde{F}(\theta) = \frac{2 \tan(\theta - \arctan \theta)}{\theta} \quad (3.6)$$

There is little distinction between $F(\theta)$ and $\tilde{F}(\theta)$ beyond the first asymptote at $\theta = 2.7437$. Denote the value of $\theta$ at the asymptotes of $\tilde{F}(\theta)$ as $\theta_1, \theta_2, \ldots, \theta_n, \ldots$. From (3.6) the sequence of $\theta_n$ satisfies

$$\theta_n - \arctan \theta_n = n\pi - \frac{\pi}{2}, \quad n = 1, 2, \ldots \quad (3.7)$$

Note that the derivative of this function is $\theta^2/(\theta^2 + 1) \approx 1$, for $\theta^2 \gg 1$. Hence, the following recursion formula applies:

$$\theta_{n+1} - \theta_n \approx \pi, \quad \theta^2 \gg 1 \quad (3.8)$$
and the occurrence of the singularities of $\tilde{F}(\theta)$ is periodic, with period $\approx \pi$, for $\theta^2 \gg 1$. It is clear that values of $\varepsilon_{rp}$ that satisfy (4.36) exist for several values of $\theta$.

Considering $f \leq 0.3$, $\varepsilon'_{re}$ is negative above any resonance defined by (4.36), over a bandwidth that can be determined from the inequality \[ -\frac{1}{\varepsilon_r^2} \left(\frac{2 + f}{1 - f}\right) < F(\theta) < -\frac{2}{\varepsilon_r^2} \left(\frac{1 - f}{1 + 2f}\right) \] (3.9)

where $\varepsilon_r^* = \varepsilon_r^2/\varepsilon_r^1$. The lower bound is derived from the position of the resonance, (4.36), and the upper bound from the condition $\varepsilon_{re} = 0$ applied to (4.35).

The relationship between frequency $\nu$ and parameter $\theta$ is

$$\nu = c\theta / \left[2\pi a \varepsilon'_{r2}\sqrt{\mu'_{r2}}\right]$$ (3.10)

where $c$ is the speed of light in vacuum. Let’s say that the composite exhibits DNG behavior over the interval $(\nu^-, \nu^+)$, for the $n$th resonance, corresponding to $(\theta^-_n, \theta^+_n)$ via (3.10). The interval $(\theta^-_n, \theta^+_n)$ decreases as $n$ increases.

To investigate the frequency band that exhibits DNG behavior in more detail, write

$$F^- < F(\theta) < F^+ < 0$$ (3.11)

where

$$F^- = -\frac{1}{K^-} \left(\frac{2 + f}{1 - f}\right), \quad F^+ = -\frac{2}{K^+} \left(\frac{1 - f}{1 + 2f}\right)$$ (3.12)

and $K^- = \max(\varepsilon'_r, \mu'_r)$, while $K^+ = \min(\varepsilon'_r, \mu'_r)$. In Fig. 3.2, $F^-$ and $F^+$ are plotted as a function of volume fraction $f$, for $K^- = K^+ = 1, 2$ and 9. It can be seen that the interval $(F^-, F^+)$ increases as $f$ increases, but decreases with increasing $K^\pm$. This observation agrees with one made in [8] that reducing the permittivity of the particles increases the DNG frequency range.

Next, denote the points of intersection of $F(\theta)$ with $F^\pm$ by $\theta^\pm_n$, where

$$\theta^\pm_n = \theta_n + \Delta^\pm_n.$$ (3.13)

Then, the length of the $n$th interval $L_n$ over which $\varepsilon'_{re}$ or $\mu'_{re}$ is negative can be denoted as

$$L_n = \theta^+_n - \theta^-_n = \Delta^+_n - \Delta^-_n.$$ (3.14)
Figure 3.1: Array of homogeneous spheres with radius $a$, medium 2, arranged on the nodes of a simple-cubic lattice with lattice constant $p$, and embedded in a supporting matrix, medium 1.

Figure 3.2: Bounding values of $F(\theta)$, $F^-$ and $F^+$, equation (3.12) plotted as a function of volume fraction $f$. 
The interval length \( L_n \) can be connected to frequency bandwidth \( \Delta \nu_n = \nu_n^+ - \nu_n^- \) via (3.10) and (3.14).

### 3.2.2 Approximation \( k_1 a < \pi/10 \)

The dipolar approximation of Mie theory is based on the long wave approximation that the wavelength in the matrix is large compared with the dimension of the particles. The following condition is sufficient to satisfy the long-wave approximation:

\[
\frac{\lambda_1}{2a} = \frac{\lambda_0}{2a|\sqrt{\varepsilon_r^\prime \mu_r^\prime}|} > 10 \tag{3.15}
\]

where \( \lambda_1 \) is the wavelength in the matrix. Equivalently, \( k_1 a < \pi/10 \). Condition (3.15) also satisfies the restriction of effective medium theory that only one Floquet-Bloch mode is permitted in this simple cubic structure. See [7] for a more detailed discussion on this point.

Now, (3.3) can be rederived by analyzing scattering at a sphere and including the effect of \( k_1 a \) to give (3.16). This is distinct from inclusion of multipole effects in an effective medium formula, as in [14]

\[
\varepsilon_{rp} = \frac{\varepsilon_r^2 F(\theta)[2 - A(k_1 a)] + A(k_1 a)G(k_1 a) - 2}{1 - \varepsilon_r^2 F(\theta)[1 + A(k_1 a)] + A(k_1 a)G(k_1 a)} \tag{3.16}
\]

where functions \( A(\alpha) \) and \( G(\alpha) \) take the form

\[
A(\alpha) = (\alpha^2 - 1) \cos \alpha - \alpha \sin \alpha \tag{3.17}
\]

\[
G(\alpha) = \frac{2(\alpha \sin \alpha + \cos \alpha)}{\alpha^2 \cos \alpha - \alpha \sin \alpha - \cos \alpha} \tag{3.18}
\]

shown in Fig. 4.3. We now employ (3.16) to investigate the percentage DNG bandwidth achievable for various \( \varepsilon_{r_2}^\prime \) and \( \mu_{r_2}^\prime \).

### 3.2.3 Percentage Bandwidth for which \( \varepsilon_{re}^\prime < 0 \) and \( \mu_{re}^\prime < 0 \)

In Fig. 3.4(a), the percentage DNG bandwidth (defined as \( B = \frac{2|f_{max} - f_{min}|}{f_{max} + f_{min}} \times 100\% \), where \( f_{max} \) and \( f_{min} \) are the maximum and minimum frequencies bounding the DNG band respectively), is plotted for \( f = 0.3 \) as a function of \( \varepsilon_{r_2}^\prime = \varepsilon_{r_2}/\varepsilon_{r_1} \) and \( \mu_{r_2}^\prime \), predicted according to (3.16). In this calculation for \( f = 0.3 \), the maximum achievable DNG bandwidth is \( \approx 7.4\% \).
for $\varepsilon_r^{\prime\prime} = \mu_r^{\prime\prime} \approx 14$. According to the method of [15], it can be calculated that DNG behavior is extinguished for $\varepsilon_r^{\prime\prime} = \mu_r^{\prime\prime} \approx 14$ if particle magnetic loss tangent $\tan \delta_\mu = \mu''/\mu' \geq 0.0714$.

The analytical results are validated by comparison with the result of calculations made according to the method presented in [11], in which the effective constitutive parameters are obtained from exact solutions for dispersion relations of electromagnetic waves propagating on periodic arrays of magnetodielectric spheres, shown in in Fig. 3.4(b). Also shown in Fig. 3.4(b) are results determined using the Clausius-Mossotti mixing formula after obtaining the effective parameters of particles according to [11]. Further, the effective permittivity and permeability of the system with $\varepsilon_r^{\prime\prime} = \mu_r^{\prime\prime} = 45$ calculated by analytical formulas presented here and the method of [11] are compared in Fig. 3.5, and good agreement is observed although a small shift in the resonant frequency appears according to the calculation method [11].

### 3.3 Conclusion

Based on Mie scattering theory and effective medium theory, simple analytic formulas for achievable DNG bandwidth are provided for a cubic array of identical, non-metallic, magnetodielectric spherical inclusions embedded in a supporting matrix according to the approximations $k_1a \to 0$ and $k_1a < \pi/10$. From the analysis, the maximum achievable DNG bandwidth for a simple cubic system with particle volume fraction $f = 0.3$ is 7.4% for particles with permittivity and permeability 14 times larger than that of the matrix.

### 3.4 Acknowledgment

The authors thank Yang Li for performing calculations according to the method of [11].
Figure 3.3: Functional behavior of $G(k_1a)$ and $A(k_1a)$ versus $k_1a$. 

(a)
Figure 3.4: Percentage achievable DNG bandwidth plotted (a) as a function of $\varepsilon_{r2}^*$ and $\mu_{r2}^*$, according to (3.16), and (b) calculated for $\varepsilon_{r2}^\prime = \mu_{r2}^\prime$ using (3.3), (3.16), and by the method presented in [8]. $f = 0.3$.

Figure 3.5: Effective permittivity and permeability of a simple cubic lattice of spheres with $\varepsilon_{r2}^\prime = \mu_{r2}^\prime = 45$ versus $k_1a$ calculated according to (3.3), $k_1a \to 0$, (3.16), $k_1a < \pi/10$, and by the method presented in [8]. $f = 0.3$. 
References


CHAPTER 4. Design of coated spheres for isotropic double-negative metamaterials

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Based on the dipole approximation of Mie theory, which describes scattering of an electromagnetic plane wave by a sphere, and on effective medium theory, an explicit analytic expression for the effective permittivity $\varepsilon_e$ or permeability $\mu_e$ of a simple-cubic array of coated spheres in a matrix is derived by the method of Hertz potential expansions. Inter-particle multipole interaction terms are included for improved accuracy at higher particle volume fractions. The derived expressions are used to guide the process of tuning the particle core-shell radius ratio under physical restrictions in order to choose a suitable combination of dielectric core and conductive shell parameters to achieve the largest possible double-negative (i.e. negative real $\varepsilon_e$ and $\mu_e$) bandwidth at terahertz frequencies.

DNG materials, Hertz potentials, multipole, NIM.

4.1 Introduction

For many applications such as antennas, waveguides and optical lenses, it is desirable to engineer materials that have the ability to localize electromagnetic waves and manipulate electromagnetic radiation [1]. This can be achieved by control of the dielectric and magnetic properties of the material, since these control the material’s interaction with the electromagnetic field associated with propagating radiation.
Assuming that the time-dependence of the electromagnetic waves takes the form \( \text{Re}[\exp(-i\omega t)] \), the following notation is adopted for material linear permittivity \( \varepsilon \) and permeability \( \mu \),

\[
\varepsilon = \varepsilon_0 (\varepsilon'_r + i\varepsilon''_r) \quad \text{and} \quad \mu = \mu_0 (\mu'_r + i\mu''_r),
\]

(4.1)
in which \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free space, respectively, and the subscript \( r \) denotes relative parameters. The term ‘double negative’ (DNG) indicates that the following conditions hold simultaneously,

\[
\varepsilon'_r < 0 \quad \text{and} \quad \mu'_r < 0.
\]

(4.2)

These conditions together imply that the real part of the refractive index is negative, \( n' < 0 \) [2].

Many present realizations of artificial DNG materials rely on the controlled spatial arrangement of especially-shaped metallic circuit elements [3][4]. In contrast with this approach, simple composite systems consisting of dispersions of non-metallic particles offer the possibility of realizing DNG behavior, in which case there may be no need for structured assembly of shaped circuit elements. For example, it has been shown that both periodic and random arrays of dielectric cylinders can compose a metamaterial with DNG properties [5]. Similarly, dispersions of homogeneous particles have been shown to exhibit \( \mu' < 0 \) [6][7].

In order to obtain DNG behavior according to Eqn. (4.2), it is necessary that the frequency bands for which both \( \varepsilon'_r < 0 \) and \( \mu'_r < 0 \) must overlap. This is difficult to achieve in a system of homogeneous dielectric particles, however, and some authors have considered mixing two types of dielectric spheres in a matrix; one to support \( \varepsilon'_r < 0 \) and the other for \( \mu'_r < 0 \) [8][9][10]. The use of an array of identical homogeneous magneto-dielectric particles to achieve DNG behavior has also been proposed [11], but high values of particle permittivity and permeability are needed, which may be difficult to achieve in practice. In order to achieve DNG behavior in a composite formed by a dispersion of spheres, then, one can consider blending dielectric and magnetic materials either as separate particles within a supporting matrix, as done theoretically in Refs. [12] and [13], or by special engineering of the particle. Here, design of a coated particle is considered in order to achieve DNG behavior in a mixture filled with such identical particles.
Previously, a core-shell non-magnetic particle composite was proposed by Wheeler et al [14], in which both Mie resonances of the dielectric core and plasma resonances of the plasmonic shell are exploited to achieve DNG behavior. In [15], core-shell systems with double-negative, single-negative, and/or double-positive metamaterial layers were investigated theoretically. Practically, metallic nanoshells as nano-scale core-shell particles have also drawn much interest in recent years, and they possess tunable properties due to the hybrid plasma resonances studied in [16][17].

Here, we discuss a range of potentially-realizable core-shell particles that are, theoretically, predicted to exhibit DNG behavior. First, rather than adopting the standard numerical evaluation of the Mie formulas for coated spheres, the theoretical formulas for the effective permittivity and permeability of a composite medium consisting of coated spheres embedded in a matrix are derived based on a Hertz-potential formulation under the dipole approximation [18]. The resulting particle polarizability is then combined with a modified effective medium theory. Practical combinations of real materials that could be used to fabricate core-shell DNG materials are then suggested. As a guide to future experimental developments, an effective procedure is given for design of materials exhibiting maximum DNG bandwidth in the TeraHertz frequency region.

4.2 Theory

4.2.1 Scattering by a Coated Sphere

Throughout this paper, a simple-cubic arrangement of coated spheres is considered, as shown in Fig. 4.1. The rigorous analytical solution for scattering of a plane wave by a sphere was first given by Mie [19] and more recently by Stratton [20] and others [21]. The solution for the electromagnetic scattering parameters is expressed in terms of different kinds of Bessel functions with complex arguments. These are complicated to evaluate numerically [22], making it more difficult to analyze such systems in order to select the best physical parameters for design of practical materials. Alternatively, a simple analytic lower-order solution of this problem can be derived by adopting the Hertz-potential representation of the electromagnetic
fields. In this way, scattering by a homogeneous sphere was initially studied by Lewin [23]. Subsequently, Galstyan et al. [18] extended Lewin’s approach to the case of two-layer spheres. Galstyan’s solution was built on the assumption \( k_1a \to 0 \), however, in which \( k_1 = \frac{2\pi}{\lambda_1} \) is the wave number in the matrix, \( \lambda_1 \) is the wavelength in the matrix and \( a \) is the radius of the sphere. Here, an improved solution of the scattering of a plane wave by a two-layer sphere is presented, with terms of order \( k_1a \) retained under the restriction \( k_1a < 1 \) which allows simplification of the scattering problem by approximation of the layered spherical scatterer as a dipolar source.

Assume that the incident electromagnetic wave propagates along the \( z \)-axis, that the transverse electric field \( \mathbf{E} \) is parallel to \( x \)-axis, and the transverse magnetic field \( \mathbf{H} \) is parallel to \( y \)-axis. Then the incident fields in the matrix, region 1 (Fig. 4.1), can be written in the following forms:

\[
\mathbf{E}_1 = \hat{x}E_{0x}e^{ik_1z} \quad \text{and} \quad \mathbf{H}_1 = \hat{y}H_{0y}e^{ik_1z}. \tag{4.3}
\]

In a source-free region, the fields can be expanded in terms of the electric Hertz potential \( \Psi \) and magnetic Hertz potential \( \Pi \) [24],

\[
\mathbf{E}_i = (\nabla \nabla \cdot + k_i^2)\hat{x}\Pi_i - i\omega\mu_i\nabla \times \Psi_i, \tag{4.4}
\]

\[
\mathbf{H}_i = (\nabla \nabla \cdot + k_i^2)\hat{y}\Psi_i - i\omega\varepsilon_i\nabla \times \Pi_i, \tag{4.5}
\]

in which \( i = 1, 2, 3 \) represents the three regions of the system (matrix, particle coating and core respectively).

The following development is in terms of the electrical properties of the system. An analogous development holds for the magnetic properties. The scattered electric field \( \mathbf{E}_i^s \) due to the electric dipole, represented by superscript \( e \), is given by the first term on the right-hand-side of Eqn. (4.4). That due to the magnetic dipole, \( \mathbf{E}_i^m \), represented by superscript \( m \), is given by the second term on the right-hand-side of Eqn. (4.4) so that \( \mathbf{E}_i = \mathbf{E}_i^s + \mathbf{E}_i^m \). Assuming that the scattered field can be approximated by that due to a dipole, the forms of \( \Pi_i \) and \( \Psi_i \) become simplified such that \( \Pi_i = \hat{x}\Pi_{ix}, \Psi_i = \hat{y}\Psi_{iy} \) and both have radial dependence \( e^{ik_ir}/r \). Then

\[
\mathbf{E}_i^s = (\nabla \nabla \cdot + k_i^2)\hat{x}\Pi_{ix} = \left( \frac{\partial^2}{\partial x^2} + k_i^2 \right)\hat{x}\Pi_{ix}, \tag{4.6}
\]
\[ E_{1}^{m} = -i\omega \mu_{ri} \nabla \times (\hat{y}\Psi_{iy}) = i\omega \mu_{ri} y \frac{\partial\Psi_{iy}}{\partial z} \]  
(4.7)

and the electric field scattered by a particle located at the origin of the spherical coordinate system, assuming that the observation point is located at distance \( r \) from the origin, is written as

\[ E_{1}^{e} = A \left( \frac{\partial^2}{\partial x^2} + k_{1}^2 \right) \frac{e^{ik_{1}r}}{r} \hat{x}. \]  
(4.8)

Similarly, the electric field in region 2 due to the electric dipole can be expressed as:

\[ E_{2}^{e} = A' \left( \frac{\partial^2}{\partial x^2} + k_{2}^2 \right) \frac{\cos k_{2}r}{r} \hat{x} + C' \left( \frac{\partial^2}{\partial x^2} + k_{2}^2 \right) \frac{\sin k_{2}r}{r} \hat{x}, \]  
(4.9)

and that in region 3 is

\[ E_{3}^{e} = C \left( \frac{\partial^2}{\partial x^2} + k_{3}^2 \right) \frac{\sin k_{3}r}{r} \hat{x}, \]  
(4.10)

where \( A, A', C' \) and \( C \) are coefficients to be determined by the boundary conditions and \( k_{1}, k_{2} \) and \( k_{3} \) are wave numbers in the matrix, shell and core regions, respectively.

The coefficient \( A \) is defined as the strength of the electric dipole, which takes the form,

\[ A = \frac{E_{0x} a^{3} \varepsilon_{p} - \varepsilon_{1}}{\varepsilon_{p} + 2\varepsilon_{1}} = \frac{E_{0x}}{4\pi} \alpha_{e}. \]  
(4.11)

Similarly, the strength of the magnetic dipole \( B \) is given by

\[ B = \frac{H_{0y} a^{3} \mu_{p} - \mu_{1}}{\mu_{p} + 2\mu_{1}} = \frac{H_{0y}}{4\pi} \alpha_{m}, \]  
(4.12)

in which \( H_{0y} = E_{0x}/\eta_{1} \) for the incident TEM plane wave, \( \varepsilon_{p} \) and \( \mu_{p} \) are the equivalent permittivity and permeability of the core-shell particle, respectively, \( \eta_{1} = \sqrt{\mu_{r1}/\varepsilon_{r1}} \) is the impedance of the matrix and \( \alpha_{e} \) and \( \alpha_{m} \) are electric and magnetic polarizabilities, respectively. Therefore, the ratio between the strength of the magnetic dipole and the strength of the electric dipole is

\[ \frac{A}{B} = \frac{\alpha_{e}}{\eta_{1} \alpha_{m}}. \]  
(4.13)

Eqn. (4.13) relates the value of \( A/B \) to the ratio between the electric and magnetic polarizabilities, which will be used in justifying neglecting the contribution of the magnetic Hertz potential \( \Psi_{i} \) to the electric field, near the electric resonance.
Due to the spherical geometry of the inclusion, the forms of the fields and Hertz potentials are transformed from Cartesian coordinates to spherical coordinates according to the following relations,

\[
\begin{align*}
\mathbf{E}_r & = E_x \sin \theta \cos \varphi, \quad \mathbf{H}_r = H_y \sin \theta \sin \varphi, \\
\Pi_r & = \Pi_x
\end{align*}
\]  \hspace{1cm} (4.14)

\[
\begin{align*}
\mathbf{E}_\theta & = E_x \cos \theta \cos \varphi, \quad \mathbf{H}_\theta = H_y \cos \theta \sin \varphi, \\
\Pi_\theta & = \Pi_x
\end{align*}
\]  \hspace{1cm} (4.15)

\[
\begin{align*}
\mathbf{E}_\varphi & = -E_x \sin \varphi, \quad \mathbf{H}_\varphi = H_y \cos \varphi, \\
\Pi_\varphi & = \Pi_x
\end{align*}
\]  \hspace{1cm} (4.16)

Transforming Eqn. (4.6) gives

\[
\mathbf{E}_i^e = \hat{r} \sin \theta \cos \varphi \left( k_i^2 + \frac{\partial^2}{\partial r^2} \right) \Pi_{ix} + \hat{\theta} \cos \theta \cos \varphi \left( k_i^2 + \frac{1}{r} \frac{\partial}{\partial r} \right) \Pi_{ix}
\]

\[
- \hat{\varphi} \sin \varphi \left( k_i^2 + \frac{1}{r} \frac{\partial}{\partial r} \right) \Pi_{ix},
\]  \hspace{1cm} (4.17)

while the scattered electric field \( \mathbf{E}_m^i \) due to the magnetic dipole in spherical coordinates is,

\[
\mathbf{E}_m^i = -i \omega \mu_r \nabla \times \Psi_i = -i \omega \mu_r \left( -\cos \varphi \frac{\partial \Psi_{iy}}{\partial \theta} + \cos \theta \sin \varphi \frac{\partial \Psi_{iy}}{\partial r} \hat{\varphi} \right).
\]  \hspace{1cm} (4.18)

For convenience in the following analysis, define parameters \( \xi_1, \xi_{2a}, \xi_{2b} \) and \( \xi_3 \) as,

\[
\begin{align*}
\xi_1 & = k_0 a \sqrt{\varepsilon_r \mu_r}, \quad \xi_{2a} = k_0 a \sqrt{\varepsilon_2 \mu_r}, \\
\xi_{2b} & = k_0 b \sqrt{\varepsilon_2 \mu_r}, \quad \xi_3 = k_0 b \sqrt{\varepsilon_3 \mu_r}.
\end{align*}
\]  \hspace{1cm} (4.19)

From Eqn. (4.18), we can see that the electric fields \( \mathbf{E}_m^i \) arising from the magnetic dipole contain only components tangential to a sphere whose surface is defined by \( r = \text{constant} \). Further, \( \mathbf{E}_m^i = 0 \) within the particles under the dipolar approximation. Therefore, \( \mathbf{E}_m^i \) affects linear Eqns. (4.8) to (4.10) obtained by applying interface conditions only through the tangential component of the electric field at the interface \( r = a \). So, in order to apply the boundary conditions to derive the strength of the electric dipole \( A \), it can be shown that the contribution of \( \Psi_i \) is negligible by considering the ratio of the tangential components of \( \mathbf{E}_m^i \) and \( \mathbf{E}_1^e \) at
\[ r = a. \text{ Averaged over } \theta, \text{ these are} \]
\[
\left| \frac{E_{m}^{\theta}}{E_{e}^{\theta}} \right| \propto \frac{\alpha_{m}}{\alpha_{e}} |K(\xi_{1})| \quad \text{and} \quad \left| \frac{E_{m}^{\varphi}}{E_{e}^{\varphi}} \right| \propto \frac{\alpha_{m}}{\alpha_{e}} |K(\xi_{1})|, \tag{4.20}
\]

where \( K(\xi_{1}) \) is found to be
\[
K(\xi_{1}) = \frac{\xi_{1}(\xi_{1} \cos \xi_{1} - \sin \xi_{1})}{(\xi_{1}^{2} - 1) \cos \xi_{1} - \xi_{1} \sin \xi_{1}}. \tag{4.21}
\]

From relations (4.20), it can be seen that the ratio of the tangential components of \( E_{m}^{1} \) and \( E_{e}^{1} \) approaches zero when the system is close to an electric dipolar resonance, because \( \alpha_{e} \rightarrow \infty \) there. Besides, since the condition \( \xi_{1} < 1 \) is always satisfied in our cases to ensure the validity of the dipolar approximation, \( K(\xi_{1}) \) is quite small when \( \xi_{1} = k_{1}a < 1 \), which can be seen in Fig. 4.2. Therefore, to derive \( \alpha_{e} \) near the electric resonance, the contribution of the Hertz potential \( \Psi_{i} \) to the electric field can be neglected. Similarly, it can be shown that the contribution of the Hertz potential \( \Pi_{i} \) to \( \alpha_{m} \) is negligible. This approximation is also made in [18].

From Eqn. (4.11), it can be seen that the effective permittivity of the particle \( \varepsilon_{p} \) can be obtained from the expression of effective polarizability, which is contained in the expression of the coefficient \( A \). Therefore, it is necessary to derive the explicit analytic expression of coefficient \( A \) in order to obtain \( \varepsilon_{p} \). The boundary conditions require that the tangential electric fields should be continuous at the interfaces \( r = a \) and \( r = b \);
\[
A \left( k_{1}^{2} + \frac{1}{r} \frac{\partial}{\partial r} \right) e^{ik_{1}r} + E_{0x} = \left( k_{2}^{2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \left[ A' \frac{\cos k_{2}r}{r} + C' \frac{\sin k_{2}r}{r} \right], \quad r = a \tag{4.22}
\]

and
\[
\left( k_{2}^{2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \left[ A' \frac{\cos k_{2}r}{r} + C' \frac{\sin k_{2}r}{r} \right] = C \left( k_{3}^{2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \frac{\sin k_{3}r}{r}, \quad r = b. \tag{4.23}
\]

The boundary conditions also require that the normal electric flux should be continuous at the interfaces;
\[
\varepsilon_{r1} \left[ A \left( k_{1}^{2} + \frac{\partial^{2}}{\partial r^{2}} \right) e^{ik_{1}r} + E_{0x} \right] = \varepsilon_{r2} \left( k_{2}^{2} + \frac{\partial^{2}}{\partial r^{2}} \right) \left[ A' \frac{\cos k_{2}r}{r} + C' \frac{\sin k_{2}r}{r} \right], \quad r = a \tag{4.24}
\]

and
\[
\varepsilon_{r2} \left\{ \left( k_{2}^{2} + \frac{\partial^{2}}{\partial r^{2}} \right) \left[ A' \frac{\cos k_{2}r}{r} + C' \frac{\sin k_{2}r}{r} \right] \right\} = \varepsilon_{r3} C \left( k_{3}^{2} + \frac{\partial^{2}}{\partial r^{2}} \right) \frac{\sin k_{3}r}{r}, \quad r = b. \tag{4.25}
\]
Figure 4.1: Coated spherical inclusions arranged on the nodes of a simple-cubic lattice with lattice constant $p$. Medium 1 is the supporting matrix, and medium 2 is the coating on a spherical core, medium 3.

Figure 4.2: Functional behavior of $K(k_1a)$ versus $k_1a$. 
Solving linear Eqns. (4.22) to (4.25), $A$ can be obtained. Then the expression for $\varepsilon_p$ can be obtained from Eqn. (4.11). For convenience, define four functions $G(\beta)$, $F(\beta)$, $A(\beta)$ and $B(\beta)$ as

\[
F(\beta) = \frac{-2(\beta \cos \beta - \sin \beta)}{\beta^2 - 1} \sin \beta + \beta \cos \beta, \quad (4.26)
\]
\[
G(\beta) = \frac{2(\beta \sin \beta + \cos \beta)}{\beta^2 - 1} \cos \beta - \beta \sin \beta, \quad (4.27)
\]
\[
A(\beta) = (\beta^2 - 1) \cos \beta - \beta \sin \beta, \quad (4.28)
\]
\[
B(\beta) = (\beta^2 - 1) \sin \beta + \beta \cos \beta. \quad (4.29)
\]

Then the relative effective permittivity of the coated particle is expressed as

\[
\varepsilon_{rp} = \frac{\varepsilon_{\varepsilon_2} G(\xi_2a) - \varepsilon_{\varepsilon_3} F(\xi_3a)}{\varepsilon_{\varepsilon_3} F(\xi_3) - \varepsilon_{\varepsilon_2} F(\xi_2a)} M_1 + \frac{A(\xi_2a) B(\xi_2a) M_2}{A(\xi_2a) B(\xi_2a)} M_3 \quad (4.30)
\]
\[
\varepsilon_{\varepsilon_2} G(\xi_2a) - \varepsilon_{\varepsilon_3} F(\xi_3a) M_3 + \frac{A(\xi_2a) B(\xi_2a) M_2}{A(\xi_2a) B(\xi_2a)} M_4 \]

where

\[
M_1 = \varepsilon_{\varepsilon_2} F(\xi_2a)[2 - A(\xi_1)] + A(\xi_1)G(\xi_1) - 2, \quad (4.31)
\]
\[
M_2 = \varepsilon_{\varepsilon_2} G(\xi_2a)[2 - A(\xi_1)] + A(\xi_1)G(\xi_1) - 2, \quad (4.32)
\]
\[
M_3 = -\varepsilon_{\varepsilon_2} F(\xi_2a)[1 + A(\xi_1)] + A(\xi_1)G(\xi_1) + 1, \quad (4.33)
\]
\[
M_4 = -\varepsilon_{\varepsilon_2} G(\xi_2a)[1 + A(\xi_1)] + A(\xi_1)G(\xi_1) + 1. \quad (4.34)
\]

An expression similar to Eqn. (4.30) holds for the effective permeability of the coated particle $\mu_{rp}$. The solution given in [18] can be deduced from Eqn. (4.30) by assuming $\xi_1 = k_1a \to 0$, i.e. the value of $G(\xi_1)$ is taken as $-2$. This means that the solution of [18] does not account for the effect of the matrix properties on the effective permittivity of the particle. Considering the function $G(k_1a)$ shown in Fig. 4.3, it can be seen that the approximation $G(k_1a) = -2$ is not accurate when $k_1a$ is not very small. Under the dipole approximation, the restriction on the values of $k_1a$ can be taken as $k_1a < 1$. So it is necessary to take into account the effect of the matrix properties on the expression for the effective permittivity $\varepsilon_{rp}$ of coated spheres.
4.2.2 Effective Medium

As shown in Fig. 4.1, a simple-cubic structure of coated spherical inclusions is studied in this paper due to its high symmetry and mathematical convenience. The relative effective permittivity $\varepsilon_{re}$ and permeability $\mu_{re}$ of a simple-cubic lattice of homogeneous particles are derived in [23] by a lattice-sum technique, and are found to be similar in form to the Maxwell-Garnett formula. Following the same procedure, similar formulas hold for a simple-cubic lattice of coated spheres, i.e.,

$$\varepsilon_{re} = \varepsilon_{r1} \left( 1 + \frac{3f}{\varepsilon_{rp} + 2\varepsilon_{r1} - f} \right),$$

(4.35)

where $f$ is the volume fraction of the spherical inclusions, and $\varepsilon_{rp}$ in Eqn. (4.35) replaces the scalar homogeneous permittivity that appears in the Maxwell-Garnett formula. Due to the couplings of electric and magnetic fields included in Eqn. (4.30) and its counterpart for $\mu_{rp}$, resonant behavior is predicted by Eqn. (4.35) and by an equivalent expression for $\mu_{re}$ when the particle size is comparable to the wavelength in the medium. The conditions under which $\varepsilon'_{re} < 0$, which occurs just above the resonant frequency, can be derived by the combination of Eqns. (4.30) and (4.35). Similar conditions apply for $\mu_{rp}$ and $\mu'_{re}$.

Note, when $\varepsilon_{re}$ is at resonance governed by Eqn. (4.35), the value of $\varepsilon_{rp}$ satisfies

$$\varepsilon_{rp}^{\text{res}} = -\varepsilon_{r1} \left( \frac{2 + f}{1 - f} \right).$$

(4.36)

4.3 Terahertz DNG materials

In this section, constituent materials and dimensions are proposed for a composite material that is predicted to exhibit DNG behavior in the terahertz frequency range. By varying the particle radius $a$ and core-to-particle radius ratio $b/a$ over a certain range, the maximum DNG bandwidth $\Delta \nu$ can be predicted for the selected material parameters. The bandwidth $\Delta \nu$ is defined $\Delta \nu = \nu_+ - \nu_-$, where $\nu_+$ and $\nu_-$ are the upper and lower frequency bounds of the DNG frequency band, respectively.

The polaritonic material lithium tantalate (LiTaO$_3$) is selected as a suitable particle core material [14] due to its relatively large static permittivity which can be utilized to give rise to
negative effective permeability. The permittivity of LiTaO$_3$ is given by the following dispersion relation,
\[ \varepsilon_r(\omega) = \varepsilon_r(\infty) \left( 1 + \frac{\omega^2_L - \omega^2_T}{\omega^2_T - \omega^2 - i\omega\gamma} \right), \]
(4.37)
where \( \varepsilon_r(\infty) = 13.4 \) is the relative permittivity at high frequency, \( \omega_T = 26.7 \) THz and \( \omega_L = 46.9 \) THz are the transverse and longitudinal optical phonon frequencies respectively, and \( \gamma = 0.943 \) THz is the damping rate.

Silicon, being a typical semiconductor material, is selected for the particle coating. The dielectric constant is described by a modified Drude model that accounts for effects of charge carriers:
\[ \varepsilon_r(\omega) = \varepsilon_r(0) - \frac{\omega_p^2}{\omega^2 - i\omega\gamma}. \]
(4.38)
In Eqn. (4.38), the intrinsic part of the permittivity for crystalline silicon is \( \varepsilon_r(0) = 11.7 \), and the plasma frequency \( \omega_p \) and damping rate can be expressed as
\[ \omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}} \quad \text{and} \quad \gamma = \frac{\rho Ne^2}{m^*}, \]
(4.39)
where \( N \) is the doping level, \( \rho \) is the resistivity and \( m^* \) is the effective mass of the electron. From Eqns. (4.38) and (4.39), the values of the plasma frequency and the damping rate are proportional to \( N \) and \( \sqrt{N} \), respectively. From Table I in Ref. [25], which lists the values of \( \omega_p \) and \( \gamma \) for silicon with various doping levels, silicon with \( N = 1.3 \times 10^{18} \) cm$^{-3}$ is adopted for the particle coating. For this doping level, the plasma frequency and damping rate have values \( \omega_p = 110.18 \times 10^{12} \) rads$^{-1}$ and \( \gamma = 76.88 \) THz, respectively. Similar coated spheres have been proposed previously [14] although in that case the ratio \( \gamma/\omega_p \) and the intrinsic part of the permittivity \( \varepsilon_r(0) \) for silicon were assumed to be 1/100 and 1 respectively, somewhat different from the experimentally-determined values mentioned above.

### 4.3.1 Comparative Example

First, to verify our formulation, we use the same physical parameters of the lattice used in generating results shown in Fig. 3 of [14] for comparison, and plot the effective refractive index \( n_e \) in Fig. 4.4.
Figure 4.3: Functional behavior of $G(k_1a)$ versus $k_1a$.

Figure 4.4: The effective refractive index of a collection of coated spheres calculated using Eqn. (4.35) (dipolar approximation). The spherical LiTaO$_3$ core has radius $b = 4$ µm, and the coatings are a Drude material with $a = 4.7$ µm, $\omega_p/(2\pi) = 4.22$ THz, and $\gamma = \omega_p/100$. The filling fraction is $f = 0.435$. 
The effective refractive index \( n_e \) is here determined from computed values of \( \varepsilon_{re} \) and \( \mu_{re} \) according to the relation

\[
n_e = \sqrt{\varepsilon_{re}\mu_{re}}.
\] (4.40)

The result shown in Fig. 4.4 is similar to that of [14] although the magnitude shown here is slightly larger than that predicted in [14]. Our theory reduces to Lewin’s model [23] by letting \( b = a \) in the formulas presented here, and the formula derived in [23] is widely accepted [11]. On the other hand, comparing the formulas presented in [26][14] (reduced for homogeneous spheres) with Lewin’s model it is found that the difference in magnitude of predicted \( n_e \) persists.

### 4.3.2 Particle Design for Maximum DNG Bandwidth

It is discussed in [11] that structures with sufficiently large \( \varepsilon''_{re} \) or \( \mu''_{re} \) do not exhibit DNG behavior due to damping of the resonances. Here, because of the relatively large loss angle of the semiconductor shells, we choose to restrict the volume fraction of the shells in order to control the losses. For this reason, in the following calculation we choose to study the radius ratio \( b/a \) within the following range,

\[
0.5 < b/a < 1.
\] (4.41)

In addition, as discussed in chapter 2, two conditions need to be satisfied to ensure the validity of the model. One restriction is that the size of the unit cell should be smaller than the wavelength in the effective medium, i.e.

\[
\frac{\lambda_0}{\sqrt{\varepsilon_{re}\mu_{re}}} > 2p,
\] (4.42)

and the other restriction is that the wavelength in the matrix should be large compared to the spacing of the particles in the lattice, based on the assumption of the dipolar approximation of Mie theory [24];

\[
\frac{\lambda_0}{\sqrt{\varepsilon_{r1}\mu_{r1}}} > 2p.
\] (4.43)

(A similar condition can be derived from the fact that only one Floquet-Bloch mode of the simple cubic lattice is permitted under the effective medium regime.)
To achieve DNG behavior under the conditions (4.42) and (4.43), the particle radius is confined within a certain range which can be numerically determined as

\[ 1.744 \, \mu\text{m} < a < 4.212 \, \mu\text{m}. \] (4.44)

This means, for \( f = 0.5 \),

\[ 3.542 \, \mu\text{m} < p < 8.555 \, \mu\text{m}. \] (4.45)

Relation (4.45) is in accordance with the conclusion reached in [27] that there exist certain limits on the size of the lattice unit cell in order to achieve DNG behavior in periodic arrays. The ratio of the size of the unit cell to the wavelength in the matrix, \( p/\lambda \), in the published literature mostly ranges from 0.11 to 0.42 [27]. Here, relation (4.45) corresponds to

\[ 8 \, \mu\text{m} < \lambda < 77 \, \mu\text{m}. \] (4.46)

When the volume fraction is \( f = 0.5 \), the DNG bandwidth \( \Delta \nu \) in our model can be determined from the values of radius \( a \) and radius ratio \( b/a \), i.e. \( \Delta \nu(a, b/a) \). Therefore, as shown in Fig. 4.5, the DNG bandwidth can be plotted versus \( a \) and \( b/a \) within the bounds specified by (4.44) and (4.41) respectively. The observed maximum DNG bandwidth in Fig. 4.5 is 0.37 THz for \( a = 3.25 \, \mu\text{m} \) and \( b/a = 0.635 \). Using these values, \( \varepsilon_{re} \) (Eqn. 4.35), \( \mu_{re} \) (similarly), \( n_e \) (Eqn. 4.40) of the structure are computed and plotted versus frequency in Figs. 4.6 to 4.8. Both DNG and negative index behaviors are observed.

4.4 Conclusion

Based on a Hertz-potential formulation, an explicit analytic solution for the effective electromagnetic parameters of a composite material formed by embedding a simple-cubic array of coated spheres in a matrix is given, providing an effective way to determine particle dimensions to achieve maximum DNG bandwidth with specific constituent materials.

In Sec. 4.3 of this paper, the DNG behavior of a simple-cubic array of coated particles consisting of a LiTaO$_3$ core and doped silicon shell is proposed for terahertz applications. A map of the obtainable DNG bandwidth is plotted as a function of particle radius and core-shell
Figure 4.5: Contours of DNG bandwidth versus particle radius $a$ and radius ratio $b/a$ for silicon-coated LiTaO$_3$ particles, volume fraction $f = 0.5$, embedded in a supporting matrix with $\varepsilon_{r1} = X$. The scale bar at right indicates DNG bandwidth in THz.

Figure 4.6: Effective permittivity $\varepsilon_{re}$ for the simple-cubic array of spherical silicon-coated LiTaO$_3$ particles exhibiting the maximum DNG bandwidth shown in Fig. 4.5.
Figure 4.7: As in Fig. 4.6 but for effective permeability $\mu_{re}$.

Figure 4.8: As in Fig. 4.6 but for effective refractive index $n_e$. 
radius ratio. Particularly, the radius and radius ratio that correspond to the maximum DNG bandwidth for the selected materials can be determined (Fig. 4.5). Therefore, a comparatively simple theoretical mechanism for determining the DNG behavior of core-shell particle composites has been provided that can guide future experimentation.
References


CHAPTER 5. Dynamics of Polystyrene-b-Poly(methylmethacrylate) (PS-\textit{b}-PMMA) Diblock Copolymers and PS/PMMA Blends: a Dielectric Study

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The dielectric relaxation properties of poly(methyl methacrylate) (PMMA) and polystyrene-\textit{b}-poly-(methyl methacrylate) (PS-\textit{b}-PMMA) diblock copolymers were investigated by broadband dielectric spectroscopy in the frequency range from 0.01 Hz to 1 MHz and temperature range from -40 to 150 °C. By parametric fitting techniques, an \(\alpha\) relaxation process associated with the glass transition, the secondary \(\beta\) relaxation process due to localized motions of side groups, and the conductivity at low frequencies were identified and modeled for all samples. Based on the modeling results, the characteristic relaxation time, fragility index, activation energies, and relaxation strength of PMMA and PS-\textit{b}-PMMA diblock copolymers were compared. It was found that the structural \(\alpha\) relaxation of the copolymers was suppressed compared with that of PMMA. The activation energies of the localized \(\beta\) relaxation of diblock copolymers were larger than those of PMMA homopolymer and the PS/PMMA blend above the glass transition temperature. This difference is due to the existence of covalent chemical bonds that link PS and PMMA blocks together in diblock copolymers which suppress the cooperative...
structural $\alpha$ relaxation. Accordingly, the activation energy barriers of localized $\beta$ relaxations in the copolymers increase, above the glass transition temperature.

copolymers, molecular dynamics, dielectric spectroscopy, Havriliak-Negami model.

5.1 Introduction

The self-assembly of block copolymers into long-range ordered morphologies has been investigated for several decades [1]. Driven by the demand of miniaturization of devices in the microelectronics industry, they have become of great interest as a tool in nanomaterial fabrication in recent years [2-3]. Block copolymers possess favorable intrinsic properties such as long-range ordered phase separation and controllable morphology, and are relatively easy to synthesize, compared with other traditional patterning methods such as top-down lithography [4-5]. The use of block copolymer, instead of homopolymer counterparts, as the matrix in polymer-based nanocomposites affords opportunities to create tailored functional materials [6]. It is useful to understand the details of morphology changes in block copolymers under different conditions. Due to the accuracy and sensitivity of the dielectric spectroscopy technique, dielectric relaxation behaviors of copolymers are examined in this work to investigate their molecular dynamics.

Dielectric spectroscopy is a proven and sensitive technique for monitoring dynamics of polar materials over a broad temperature and frequency range, as the permittivity changes in response to phase transitions such as the glass transition [7-8]. By observing the dielectric relaxation behavior of polymers, their molecular dynamics can be studied. Dielectric spectroscopy is now widely used to investigate molecular dynamics of copolymers and nanocomposites [9-11].

Polystyrene (PS) is a non-polar polymer that is not dielectrically active due to the presence of stable phenyl side groups. For poly(methyl methacrylate) (PMMA), on the other hand, there are two main dielectric relaxation mechanisms, namely, the structural $\alpha$-type relaxation and localized $\beta$-type relaxation. The $\alpha$ relaxation arises from the motions of backbone chains, corresponding to the glass transition of the polymer. The $\beta$ relaxation is due to the localized rotational moment of the dipole vector of the ester group (O=\(\text{C-O-CH}_3\)). This localized $\beta$
relaxation is the dominant relaxation process in PMMA. The dielectric strength of the \( \beta \) relaxation increases with temperature, which may be due to the increase of free volume, thereby leading to greater motion of dipoles [12]. The linear diblock copolymer, PS-\( b \)-PMMA, consists of PS and PMMA blocks covalently connected at one end. Depending on the molecular weight (MW) of the blocks and the polymerization process, linear diblock copolymers spontaneously phase-separate to form a wide range of morphologies, including: spherical, lamellar, cylindrical and gyroid nanostructures. This phase-separation offers, in turn, opportunity to confine nanoparticles to a particular phase, thereby controlling spatial distribution of nanoparticles within the target domain.

In this paper, the molecular dynamics of linear diblock copolymer PS-\( b \)-PMMA are studied and compared with those of PMMA homopolymer and a PS/PMMA blend.

To compare the effect of the presence of PS in the diblock copolymer PS-\( b \)-PMMA, in the blend PS/PMMA, in the copolymer PS-\( b \)-PMMA (the MW of PS and PMMA are 50k and 50k, respectively) and in the blend PS/PMMA (the MW of both PS and PMMA is 50k) samples were prepared. In order to compare the effect of MW on the molecular dynamics of copolymers, another copolymer sample PS-\( b \)-PMMA with the MW of PS and PMMA of 50k and 130k, respectively, was prepared. The frequency and temperature scans of dielectric measurements were conducted in a broad range, from 0.01 Hz to 1 MHz and from -40 to 150 \(^\circ\)C, respectively. The dielectric properties of the blends and copolymers are found to be dominated by the dielectric properties of PMMA, because PS is a nonpolar polymer. The measured dielectric spectra are fitted by a sum of two Havriliak-Negami functions [13] and a conductivity term via the least-squares fitting technique [14, 15]. The comparison between PS-\( b \)-PMMA copolymers and PMMA is conducted in terms of their characteristic relaxation time, fragility index, and relaxation strength for the \( \alpha \) relaxation process, and characteristic relaxation time, activation energy, and relaxation strength for the \( \beta \) relaxation process. The study of dielectric relaxations of copolymers and homopolymers aims to explore the relaxation dynamics which depends on the morphology as well as the degree of polymerization of polymers.
5.2 Experiment

5.2.1 Sample Preparations

PMMA homopolymer and PS-\textit{b}-PMMA diblock copolymers were obtained from Polymer Source Inc. Disk-shaped samples for dielectric testing, approximately 20 mm in diameter and ranging from 0.5 to 1.25 mm thick, were formed as follows. PMMA was heated from room temperature to 150 °C, was die-pressed under 726 kg load for 5 minutes and was allowed to cool to room temperature without the load. PS-\textit{b}-PMMA diblock copolymers were heated to 180 °C for 10 minutes, were die-pressed under 454 kg load and were allowed to cool to room temperature under a 136 kg load. The PS/PMMA blend was heated to 180 °C for 30 minutes, was die-pressed under 272 kg load for 5 minutes and was allowed to cool to room temperature under the same load. The heating rate was 10 °C/min, while the samples were cooled naturally to room temperature. Following the hot pressing processes, the samples were then polished and sputtered with Ag to form electrodes on both side of the disk-shaped samples. The thickness of the samples was measured prior to sputter coating and their diameter was measured after sputter coating, using vernier calipers. In both cases, the average of 10 measurements was recorded.

The molecular weight, diameter, thickness, and volume fraction of the PS component in the samples are summarized in Table 5.1. The volume fraction of PS in PS-\textit{b}-PMMA 50k-50k and 50k-130k is similar, despite the fact that the weights of the PMMA blocks are different, because PS and PMMA have similar mass densities; 1.05 g/cm$^3$ and 1.18 g/cm$^3$, respectively. The electrode diameter (20 mm) is slightly larger than the sample diameter, which contributes to errors of around 1% in measured permittivity due to the difference in electrode and sample surface area (Table 5.1).

5.2.2 Dielectric Measurements

The complex permittivity of the samples was measured using a Novocontrol dielectric spectrometer with automatic temperature control from -40 to 90 °C with a 10 °C increment, and from 90 to 150 °C with a 5 °C increment over a frequency range from 0.01 Hz to 1 MHz.
Table 5.1: Molecular weight, volume fraction of PS ($f_{PS}$), diameter, and thickness of the disc-shaped samples used in the study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$f_{PS}$</th>
<th>Diameter (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>50k</td>
<td>0</td>
<td>19.88±0.01</td>
<td>1.25±0.01</td>
</tr>
<tr>
<td>PS</td>
<td>50k</td>
<td>1</td>
<td>19.865±0.005</td>
<td>0.94±0.01</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-50k</td>
<td>0.53±0.03</td>
<td>19.88±0.01</td>
<td>0.855±0.005</td>
<td></td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-130k</td>
<td>0.53±0.03</td>
<td>19.82±0.01</td>
<td>0.575±0.005</td>
<td></td>
</tr>
<tr>
<td>PS/PMMA 50k/50k</td>
<td>0.53±0.03</td>
<td>19.90±0.01</td>
<td>0.905±0.005</td>
<td></td>
</tr>
</tbody>
</table>

The temperature increment was reduced above 90 °C so that the glass transition could be investigated in detail. The experimentally measured imaginary parts of relative permittivity of PMMA and PS-$b$-PMMA samples (the MW of both PS and PMMA is 50K; denoted 50k-50k) are shown in Figs. 5.1 and 5.2, respectively.

5.3 Spectral Analysis

The $\alpha$ and $\beta$ relaxation processes and a conductivity term of PMMA, PS-$b$-PMMA, and PS/PMMA samples are modeled by least squares fitting techniques [14-15]. The dielectric spectrum can be expressed as the sum of $\alpha$ and $\beta$ relaxation and a conductivity term, as described by equation (1):

$$
\varepsilon^*(\omega) - \varepsilon_\infty = \sum_{p=1}^{2} \frac{\Delta \varepsilon_p}{1 + (i\omega \tau_{p,HN})^{1-\alpha_{p,HN} \beta_{p,HN}}} - i\sigma \frac{\varepsilon_0 \omega^A}{\varepsilon_0 \omega^A} \quad (5.1)
$$

where $\omega$ is angular frequency, $p = 1, 2$ denotes the two relaxation types, $\Delta \varepsilon$ is the dielectric strength, $\varepsilon_\infty$ is the permittivity well above the frequency of measurement, $\sigma$ is the conductivity, $\varepsilon_0$ is the permittivity of free space, and $\tau_{H,N}, \alpha_{H,N}$ and $\beta_{H,N}$ are characteristic relaxation time and shape parameters that describe the Havriliak-Negami function [13]. The term containing the power $A$ is due to conductivity and electrode effects. $A$ is always smaller than 1. It is common to proceed by fitting the imaginary part of the permittivity, $\varepsilon''(\omega)$. By using the least squares fitting techniques, the fitting parameters are determined such that the following criterion is satisfied:

$$
\sum_i \left\{ \left( \frac{\varepsilon''_{exp}}{\varepsilon_0 \omega_i^A} + \frac{\sigma_{DC}}{\varepsilon_0 \omega_i^A} - \sum_{p=1}^{2} \varepsilon''_{p,HN}(\omega_i) \right)^2 \right\} \rightarrow \text{min} \quad (5.2)
$$
Figure 5.1: Experimentally measured imaginary relative permittivity $\varepsilon''$ of PMMA (MW = 50k).

Figure 5.2: Experimentally measured imaginary relative permittivity $\varepsilon''$ of PS-$b$-PMMA (50k-50k).
where the sum is over the $i$ experimental data points and

$$
\varepsilon''_{p,HN}(\omega_i) = \text{Im}\{\frac{\Delta \varepsilon_p}{1 + (i\omega \tau_{p,HN})^{1-\alpha_{p,HN} \beta_{p,HN}}}\}.
$$

An alternative approach was suggested by Turnhout and Wübbenhorst [15] in terms of the derivative $\partial \varepsilon'/\partial \omega$. This derivative method is based on the principle that each relaxation process described by Havriliak-Negami function can be decomposed into a series of Debye relaxation processes, while the relation

$$
\frac{\partial \varepsilon'_{\text{exp}}}{\partial \log \omega} = -\frac{\pi}{2} \varepsilon''_{\text{exp}}
$$

holds for each Debye relaxation processes. This derivative method was adopted in the present study, because it eliminates the effect of Ohmic contacts and provides sharper peaks in the dielectric spectrum. The corresponding criterion to that stated in Eq. (5.2) is

$$
\sum_i \left\{ \left( \frac{\partial \varepsilon'_{\text{exp}}}{\partial \log \omega} \right)_i + \frac{\sigma_{\text{DC}}}{\varepsilon_0 \omega_i^\alpha} - \sum_{p=1}^2 \frac{\partial \varepsilon'_{p,HN}(\omega_i)}{\partial \log \omega} \right\}^2 \rightarrow \text{min}
$$

(5.3)

Representative isothermal plots of PS-$b$-PMMA diblock copolymers (50k-50k and 50k-130k) are plotted at 105 °C in Fig. 5.3, where the $\alpha$ and $\beta$ relaxation processes and conductivity terms are identified. The superimposed relaxations and the conductivity term agree well with the experimental data, where the standard errors calculated according to Eq. (5.3) are $2.38 \times 10^{-4}$ and $9.89 \times 10^{-5}$ for the 50k-50k and 50k-130k diblock copolymers, respectively. Isothermal data sets were modeled at other temperatures with similar standard errors.

5.4 Results and Discussion

5.4.1 Dielectric Relaxations

5.4.1.1 Characteristic Frequency

The isochronal plots of imaginary relative permittivity of PMMA, two PS-$b$-PMMA diblock copolymers, and the PS/PMMA blend at 25 Hz are shown in Fig. 5.4. The $\alpha$ and $\beta$ relaxation processes and the effect of conductivity emerge as the temperature increases. For temperatures ranging from -40 to 80 °C, PMMA, PS-$b$-PMMA, and PS/PMMA show similar $\beta$ relaxation
peaks as the $\beta$ relaxation of PMMA dominates. As temperature increases, the corresponding $\alpha$ relaxation peaks, associated with the glass transition temperature, $T_g$, are visible for PS, PS-$b$-PMMA diblock copolymers and the PS/PMMA blends. The $\alpha$ relaxation peaks of copolymers are almost undetectable and hard to separate from the conductivity effects at the highest temperatures studied.

For amorphous polymer PMMA, the dielectric $\beta$ relaxation process arises from localized rotational fluctuations of side chains. The mechanisms of $\beta$ relaxation were discussed by Goldstein and Johari [25][26], and they argued that the $\beta$ relaxation universally exists in a great variety of amorphous polymers. The temperature dependence of the characteristic relaxation time of $\beta$ relaxation follows the Arrhenius law:

$$f_{\beta,max} = f_0 \exp\left(\frac{E_A}{k_B T}\right)$$  \hspace{1cm} (5.4)

where the factor $f_0$ is on the order of the vibrational frequency of the localized motions, $E_A$ is the activation energy of the $\beta$ relaxation, and $k_B$ is the Boltzmann constant. Above the glass transition temperature $T_g$, the glassy state is transformed to a rubbery state, which is also known as a super cooled liquid. When the temperature increases up to the melting temperature $T_m$, the super cooled liquid will transform to the liquid state. The segmental motions and chain connectivity of polymers both contribute to the dynamic glass transition by intramolecular and intermolecular cooperativity. The characteristic relaxation rate of $\alpha$ relaxation, which describes the viscosity and structural relaxation, obeys the Vogel-Fulcher-Tammann (VFT) law [16-18]

$$f_{\alpha,max} = f_0 \exp -\frac{DT_0}{T - T_0}$$  \hspace{1cm} (5.5)

where D is the strength parameter and the temperature $T_0$ is characteristic of static dipolar freezing of dipolar motion in the absence of long-range correlation. The fragility of polymers, with index m [7], is related to the curvature in the plot of $\log_{10}(f_{\alpha,max})$ versus $1/T$, is thus a measure of the steepness of the temperature dependence, and is given by

$$m = \left. \frac{d \log_{10} \frac{1}{2\pi f_{\alpha,max}}}{dT/T_0} \right|_{T=T_g}.$$  \hspace{1cm} (5.6)
Figure 5.3: Imaginary relative permittivity, $\varepsilon''_r$, of PS-$b$-PMMA diblock copolymers (50k-50k (open circles) and 50k-130k (open squares)) at 105 $^\circ$C plotted as a function of frequency.

Figure 5.4: Imaginary relative permittivity, $\varepsilon''_r$, of samples as a function of temperature measured at 25 Hz.
The fragility index $m$ of the sample can be described by the following formula [7] in terms of VFT parameters,

$$m = \frac{T_g}{T_0} \frac{DT_0}{(T_g - T_0)^2}$$  \hspace{1cm} (5.7)

The relation between the maximum relaxation time and the corresponding Havriliak-Negami parameters $\alpha_{HN}$ and $\beta_{HN}$ in Eq. (5.1) are [7]

$$f_{\alpha,\beta}^{\alpha,\beta} = f_{HN}^{\alpha,\beta} \left\{ \frac{\sin \left( \pi (1 - \alpha_{HN}) \beta_{HN} \right)}{\sin \left( \pi (1 - \alpha_{HN}) \beta_{HN} \right)} \right\}^{-1/(1-\alpha)}$$  \hspace{1cm} (5.8)

where $f_{HN}^{\alpha,\beta} = 1/(2\pi \tau_{HN}^{\alpha,\beta})$ is the characteristic frequency of the $\alpha$ and $\beta$ relaxations. Fig. 5.5 shows the Arrhenius diagram of $\alpha$ and $\beta$ relaxations of the samples and the corresponding parameters are summarized in Table 5.2. The values of $f_0$ and $D$ of the two diblock copolymers are much smaller than those of PMMA, which indicates the suppression of $\alpha$ relaxation in the copolymers as compared to PMMA. On the other hand, $f_0$ for the PS/PMMA blend is only a little less than that of PMMA. The fragility index of PS-$b$-PMMA (50k-50k) is similar to that of PMMA (50k), because $m$ for PS and PMMA is similar [7]. The fragility index of PS-$b$-PMMA (50k-50k) is, however, smaller than that of PS-$b$-PMMA (50k-130k), because the fragility of PMMA generally increases with the molecular weight [12].

The temperature dependence of the $\alpha$ and $\beta$ relaxations of samples extrapolated to higher temperature is shown in 6.6. For the PMMA sample, it can be seen that when the relaxation curves are extrapolated to higher temperature, the $\alpha$ relaxation and localized $\beta$ relaxation merge to form the $\alpha\beta$ relaxation, while the cooperative $\alpha$ relaxation of the PS/PMMA blend and of the PS-$b$-PMMA diblock copolymers (50k-50k and 50k-130k) eventually disappear when the dielectric strength associated with the $\alpha$ relaxation approaches zero. The significant suppression of the $\alpha$ relaxation in the copolymer samples is discussed in Section 5.4.1.2.

For the $\beta$ relaxation, all the samples show similar values of activation energy, because the dominant $\beta$ relaxation processes all arise from localized rotational motions of side chains of PMMA (Fig. 5.5). Fig. 5.7 shows the behavior of the $\beta$ relaxation above $T_g$. The $\beta$ relaxation activation energy of PMMA and PS/PMMA above $T_g$ is larger than that of the 50k-50k and 50k-130k diblock copolymers due to significant suppression of $\alpha$ relaxation in the dynamics
of copolymers, which lowers the activation energy of the localized motions as seen clearly in Table 5.3.

Table 5.2: Parameters of $\alpha$ relaxation process for the samples used in the study (see Eqs. (5.5) to (5.7)).

<table>
<thead>
<tr>
<th>$\alpha$ relaxation</th>
<th>$f_0$ (Hz)</th>
<th>D</th>
<th>$T_0$ (K)</th>
<th>$T_g$ (K)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>$3.97 \times 10^8$</td>
<td>2.50</td>
<td>337</td>
<td>95.4</td>
<td>131±7</td>
</tr>
<tr>
<td>PS/PMMA blends</td>
<td>$1.68 \times 10^7$</td>
<td>1.80</td>
<td>342</td>
<td>96</td>
<td>139±7</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-50k</td>
<td>$4.21 \times 10^2$</td>
<td>0.56</td>
<td>354</td>
<td>96.8</td>
<td>126±6</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-130k</td>
<td>$2.65 \times 10^2$</td>
<td>0.44</td>
<td>358</td>
<td>97.6</td>
<td>150±8</td>
</tr>
</tbody>
</table>

Table 5.3: Parameters of $\beta$ relaxation process of the samples used in the study, (Eqs. (5.5) to (5.7)).

<table>
<thead>
<tr>
<th>$\beta$ relaxation</th>
<th>$E_A$ (kJ, $T &gt; T_g$)</th>
<th>$E_A$ (kJ, $T &lt; T_g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>106±5</td>
<td>78±4</td>
</tr>
<tr>
<td>PS/PMMA blends</td>
<td>106±5</td>
<td>78±4</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-50k</td>
<td>89±4</td>
<td>75±4</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-130k</td>
<td>88±5</td>
<td>82±4</td>
</tr>
</tbody>
</table>

5.4.1.2 Dielectric Strength

The dielectric strength of $\alpha$ and $\beta$ relaxation processes as a function of temperature is shown in Fig. 5.8. It is noteworthy that the volume fraction of PS in the samples is 0.53 (Table 5.1), apart from for the PMMA sample. It is thus expected that $\Delta \varepsilon_{\alpha,\beta}$ for PMMA should be larger than for the other samples, which is indeed the case seen in Fig. 5.8.

The overall dielectric strength of the $\alpha$ relaxation, $\Delta \varepsilon_\alpha$ shown in Fig. 5.8a), of the PS-$b$-PMMA diblock copolymers (50k-50k and 50k-130k) are smaller than that of PMMA and the PS/PMMA blend. This is because $\alpha$ relaxation of the copolymers is suppressed due the chemical connectedness of the PS and PMMA blocks.

The dielectric strength of $\alpha$ and $\beta$ relaxation processes can be predicted according to the Onsager-Kirkwood-Fröhlich (OKF) theory [20-24],

$$\Delta \varepsilon \sim F_{On} g N_p^2 N_p \frac{k_B T V}{k_B TV}$$

(5.9)
Figure 5.5: Arrhenius diagrams showing the $\alpha$ relaxation at temperature above $T_g$, and their extrapolation to higher temperature using the model fit data.

Figure 5.6: Arrhenius diagram of samples. $f_{max}$ is the characteristic frequency of the maximum in the curves of $\varepsilon\tau(f)$ plotted as a function of frequency. The lines are obtained by polynomial fit to the data points.
where $F_{On} \approx 1$ the is Onsager factor, $N_p/V$ is the number of dipoles per unit volume, $\mu^2$ is the square of the permanent dipole moment, and $g$ is the Kirkwood/Frohlich correlation factor describing the interaction between dipoles with respect to ideal dipoles:

$$g = 1 + \frac{\sum_i \sum_{i<j} \mu_i \mu_j}{N \mu^2} \approx 1 + z \cos(\Psi)$$

(5.10)

where $z$ is the coordination number and $\Psi$ is the angle between the $i^{th}$ and $j^{th}$ dipole.

It can be proposed that the temperature dependence behavior of the dielectric $\alpha$ relaxation results from an increasing influence of intermolecular cross-correlation terms $\sum_i \sum_{i<j} \mu_i \mu_j$ to $\mu^2$ when temperature decreases [12, 30], which means the reorientation of a test dipole is influenced increasingly by its environment dipoles with decreasing temperature. In terms of cooperative behavior, the $\alpha$ relaxation is related to an effective dipole moment $\mu_{eff}$ which is due to increase of the size of the cooperatively rearranging regions (CRR) [31] with increasing $\mu_{eff}$ when temperature decreases [30]. Therefore, the dielectric strength of $\alpha$ relaxation decreases when the temperature goes up, indicating that the environment exerts weaker influence on the reorientation of the dipole in the cooperative regime of the $\alpha$ relaxation, as temperature increases.

The $\beta$ relaxation is ascribed to the localized rotational fluctuations of the ester group and depends on the total number of contributing dipoles. The molecular weight of PMMA homopolymer and the PMMA block in PS-$b$-PMMA (50k-50k) diblock copolymer is the same, but $\Delta_\varepsilon$ of PS-$b$-PMMA (50k-50k) shown in Fig. 5.8b) is approximately half of that of PMMA due to the reduced PMMA volume fraction in the copolymer. As suggested by OKF theory, the dielectric strength $\Delta_\varepsilon$ of PS-$b$-PMMA (50k-130k) is larger than that of PS-$b$-PMMA 50k-50k due to the larger molecular weight of PMMA in the PS-$b$-PMMA (50k-130k) diblock copolymer (i.e., higher volume fraction), thereby increasing the number of dipoles that contribute to the $\beta$-relaxation.

Considering $\Delta_\varepsilon$ in the case of PS/PMMA, as PS and PMMA are immiscible [30], the introduction of PS into PMMA to form PS/PMMA increases $\Delta_\varepsilon$. By contrast, in the case of PS-$b$-PMMA diblock copolymers, PS and PMMA chains are covalently linked and, as a result, the strength of $\beta$ relaxation of PS-$b$-PMMA (50k-50k) is weaker than that of PS/PMMA.
In the case of the $\beta$ relaxation, the number of dipoles per unit volume $N_p/V$ contributing to the relaxation increases with temperature, because $\beta$ relaxation is a thermally activated process and the angular extension of the fluctuation region increases with temperature. The temperature dependence of factor $g$ is not significant, however, which is indicated by the fact that $\beta$ relaxation can occur at low temperature where reorientation of dipole vectors can hardly occur. Therefore, the overall dielectric strength of the $\beta$ relaxation strength increases with temperature.

In the case of the $\beta$ relaxation, the number of dipoles per unit volume $N_p/V$ contributing to the relaxation increases with temperature, because $\beta$ relaxation is a thermally active process and the angular extension of the fluctuation region increases with temperature. However the temperature dependence of factor $g$ is not significant as $\beta$ relaxation can occur at low temperature where reorientation of dipole vectors can hardly occur. Therefore, the overall dielectric strength of the $\beta$ relaxation strength increases with temperature.

The dielectric strength of $\alpha$ and $\beta$ relaxation processes as a function of temperature is shown in Fig. 6.8. It is noteworthy that apart from the PMMA sample, the volume fraction of PS in the samples is 0.53 (Table 5.1), it is thus expected that $\Delta \varepsilon_{\alpha,\beta}$ for PMMA should be larger than for the other samples, which is indeed the case seen in Fig. 6.8. The overall dielectric strength of the $\alpha$ relaxation, $\Delta \varepsilon_{\alpha}$, of the PS-b-PMMA diblock copolymers (50k-50k and 50k-130k) are similar to each other and much smaller than that of PMMA and the PS/PMMA blend. This is because $\alpha$ relaxation of the copolymers is suppressed due the chemical connectivity of PS and PMMA blocks.

The $\beta$ relaxation is ascribed to the localized rotational fluctuations of the ester group and depends on the total number of contributing dipoles. It depends on the molecular weight of PMMA. The molecular weight of PMMA homopolymer and the PMMA block in PS-b-PMMA (50k-50k) diblock copolymer is the same, but $\Delta \varepsilon_{\beta}$ of PS-b-PMMA (50k-50k) is approximately half of that of PMMA due to the reduced PMMA volume fraction in the copolymer. As suggested by OKF theory, the dielectric strength $\Delta \varepsilon_{\beta}$ of PS-b-PMMA (50k-130k) is larger than that of PS-b-PMMA 50k-50k due to the larger molecular weight of PMMA in the PS-
b-PMMA (50k-130k) diblock copolymer (i.e., higher volume fraction), thereby increasing the number of dipoles that contribute to the $\beta$-relaxation.

Considering $\Delta \varepsilon_{\beta}$ in the case of PS/PMMA, as PS and PMMA are immiscible [30], the introduction of PS into PMMA to form PS/PMMA increases $\Delta \varepsilon_{\beta}$. By contrast, in the case of PS-b-PMMA diblock copolymers, PS and PMMA chains are covalently linked as a result, the strength of $\beta$ relaxation of PS-b-PMMA (50k-50k) is weaker than that of PS/PMMA.

### 5.4.2 Conductivity

In the low-frequency and high-temperature regimes of the spectrum, both $\varepsilon'$ and $\varepsilon''$ exhibit high values, which are not only attributed to conductive properties of the sample, but also arise from the electrode polarization effects due to space charges building up at the interface between the sample and the electrodes. To extract the DC and AC conductivity effects, the dielectric spectrum in terms of complex permittivity $\varepsilon^*$ may be transformed into the complex conductivity $\sigma^*$ spectrum according to the relationship

$$\sigma^* = \sigma' + i\sigma'' = i\omega\varepsilon_0\varepsilon^*.$$

The real part of the conductivity is plotted as a function of frequency in Fig. 5.9 for two samples at temperatures above 132 °C. The observed behavior may be described as proposed by Jonscher [19]; the conductivity is expressed as the sum of DC and AC terms and the AC conductivity obeys a power law dependence on frequency:

$$\sigma(\omega) = \sigma_{DC} + \sigma_{AC}(\omega) = \sigma_{DC} + Z\omega^A$$

(5.11)

where $0 < A \leq 1$ and $Z$ is a frequency-independent constant of the AC conductivity term.

It can be seen from Fig. 5.9 that the conductivity tends to a constant value as frequency tends to zero. The constant, limiting value is generally regarded as the DC conductivity.

The motion of charge carriers driven by the electrical field forms a current, which can be described by $W = \mu E$, where $W$ is the drift velocity, $\mu$ is the mobility and $E$ is the electric field.

Defining $\Delta E$ as the energy gap between the conductance and valence bands, then the change in conductivity due to a change in temperature, $T$, may be attributed to a change in
mobility by invoking a thermally activated mobility according to

$$\mu = \mu_0 \exp \left( -\frac{\Delta E}{kT} \right)$$  \hspace{1cm} (5.12)

As for the frequency-dependence of the $\beta$ relaxation, Eq. (5.4), the values of DC conductivity generally follow the VFT law:

$$\sigma_{DC} = \sigma_0 \exp \left( -\frac{A}{T - T_0} \right),$$  \hspace{1cm} (5.13)

which indicates that the transport mechanism in charge-carrying polymers is associated with the motions of polymeric chains [32], which is described by Eq. (5.12). The fitting parameters according to Eq. (5.13) are listed in Table 5.3 for PMMA and the copolymers studied here.

Table 5.4: Fitting parameters of VFT law that describe DC conductivity terms of PMMA and copolymers.

<table>
<thead>
<tr>
<th>DC conductivity</th>
<th>$\sigma_0$ (S/m)</th>
<th>$A$</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>$5.39 \times 10^{-4}$</td>
<td>1985</td>
<td>283</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-50k</td>
<td>$5.15 \times 10^{-6}$</td>
<td>1075</td>
<td>330</td>
</tr>
<tr>
<td>PS-$b$-PMMA 50k-130k</td>
<td>$1.99 \times 10^{-1}$</td>
<td>3584</td>
<td>257</td>
</tr>
</tbody>
</table>

This analysis permits extraction of the DC and AC conductivity terms from the dielectric spectrum, revealing more clearly the dielectric relaxation processes and improving the accuracy of fitting the relaxations by reducing the effects of electrode polarization.

5.5 Conclusion

The dielectric spectrum of PMMA homopolymer, and PS-$b$-PMMA diblock copolymers (50k-50k and 50k-130k) and a PS/PMMA blend were investigated by broadband dielectric spectroscopy. The experimental results were modeled as the superposition of $\alpha$ and $\beta$ relaxation processes and a conductivity term. The comparison of dielectric relaxation properties of PMMA and PS-$b$-PMMA diblock copolymers was conducted in terms of the characteristic relaxation time, fragility index, activation energies, characteristic relaxation time, and relaxation strength. It was found that $\alpha$ relaxation is greatly suppressed in PS-$b$-PMMA, due to the
change of local molecular dynamics. By ext, the $\alpha/\beta$ merging process was observed only in the PMMA sample. To account for the different values of dielectric strength, changes of molecular dynamics of samples were discussed on the basis of the OKF theory. The conductivity effects were decomposed into the sum of DC and AC conductivity terms, indicating that the transport mechanism of charge carriers of DC conductivity is associated with the motions of polymeric chains.

5.6 Acknowledgment

We gratefully acknowledge funding support from the Air Force Office of Scientific Research (FA9550-09-1-0388).
References


Figure 5.7: Arrhenius diagram showing the $\beta$ relaxation above $T_g$. 
Figure 5.8: Dielectric relaxation strength of $\alpha$ relaxation of samples as a function of inverse temperature above $T_g$. Uncertainties were assumed in accordance with the confidence level of the fit between the experimental data and the model [Eq. (5.1)], which is around 5%.
Figure 5.9: Real conductivity as a function of frequency at temperatures above 132 °C.
CHAPTER 6. Plasticization and Reinforcement in Boron Cage Compounds: a Dielectric Study

A paper is to be submitted to
Journal of Non-Crystalline Solids
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1: Department of Materials Science and Engineering, Iowa State University
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Operated by Honeywell Federal Manufacturing & Technologies, LLC

In order to control and modify the properties of nanocomposite systems, it is essential to understand the nano-filler/polymer interactions. Boron cage compounds (BCCs) are a class of icosahedral, closed cage molecules that are used as nano-fillers to improve the neutron absorbing/shielding property of the composite. When the BCC is blended with a polyurethane (PU)/polybutadiene (PBD) segmented copolymer, reinforcement and plasticization of the PBD and PU segments, respectively, is observed. To investigate the effect of the n-hexylcarborane content on plasticization of PBD and reinforcement of PU, the dielectric relaxation properties of three samples, EN8 segmented polyurethanes with 0 and 5\% n-hexylcarborane by weight, were investigated by the method of broadband dielectric spectroscopy in the frequency range from 0.01 to 1 MHz and temperature range from -140 to 130 °C. By parametric fitting techniques, two $\alpha$ relaxation processes associated with the glass transition of soft PBD segments and hard urethane segments, and the secondary $\beta$ relaxation process due to localized motions of side groups, and the conductivity at low frequencies were identified and modeled for all the samples. An interfacial polarization (Maxwell-Wagner-Sillars) relaxation does not appear
due to the absence of a crystalline phase in the samples according to results differential scanning calorimetry. The relaxation map (Arrhenius diagram) associated with these processes is developed from the experimental data to elucidate the role of BCCs in the molecular dynamics of the system. Values of fitting parameters, calculated glass transition temperature, and fragility index are also given for comparison. Reduced localized motion and plasticization of soft PBD segments, as well as reinforcement of hard urethane segments, are observed with the introduction of the n-hexylcarborane. The hypothesis that the n-hexylcarborane content preferentially locates within the hard urethane segments is supported by the observed decrease of the fragility index and glass transition temperature of the urethane segments.

6.1 Introduction

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. At low temperatures, the properties of cross-linked elastomers are exhibited, which exhibit hydrogen bonded and cross-linked, phase-separated urethane blocks. This phase separation gives rise to hard ‘glassy’ domains dispersed in soft ‘rubbery’ matrix, which leads to the elastomeric properties of segmented polyurethanes. The soft segment is often a polyether or polyester of molecular weight between 1000 and 5000 possessing a glass transition temperature \( T_g \) well below ambient temperature. The hard segments are typically formed by the extension of an aromatic diisocyanate with a low molecular weight diol or diamine and have a \( T_g \) or melting transition above the usage temperature. The hard segment domains provide crosslinking, act as reinforcing fillers and are responsible for the increasing of thermal stability, stiffness and Young’s modulus of these materials at higher temperatures [1]. A schematic diagram showing possible crosslink structures and phase separation of polyurethanes is shown in Figure 6.1. The soft and hard segments of the samples studied in this work are polybutadiene (PBD) and...
polyurethane (PU) respectively.

Segmented copolymers consist of (AB)_n type alternating blocks, and their properties are affected by the intrinsic properties of the segments, the segment length, the compatibility of the segments, the polymerization method, and the ability of the blocks to crystallize. Segmented copolymers can range from random copolymers to thermoplastic elastomers. The former has been found in copolymers with short segment lengths and similar inter- and intra-segment binding forces, and those compatible copolymers exhibit homogeneous morphology. Incompatible segmented copolymers are a class of thermoplastic elastomers that exhibit phase separation. At their typical working temperature, one block is usually flexible and rubbery, while the other is hard and glassy. This leads to them being known as 'soft' and 'hard' segments as mentioned above. The unique properties of segmented copolymers arise from their particular morphology, in which the hard segments act as the reinforcing filler. As a consequence of fabrication and processing methods, however, the phase separation may be incomplete, leading to interfacial regions where a gradient of composition occurs. The two-phase microstructure of (AB)_n segmented copolymers arises from thermodynamic incompatibility of the unlike blocks. To characterize the morphology or the structure-property relationships, electron microscopy and dielectric spectroscopy are both useful, whereas dielectric spectroscopy is proven effective in characterizing temperature- and frequency-dependent behavior. Because polar groups exist in both the soft and hard segments of segmented polyurethanes, dielectric spectroscopy is a natural and effective method to investigate their relaxation behaviors, which provide insight into their molecular dynamics. Boron cage compounds (BCCs) are discrete, symmetrical, icosahedral closed cage molecules. They can be highly stable, are non-toxic and are chemically modifiable, making them attractive for potentially providing reinforcement in polymer systems.
Figure 6.1: Possible crosslink structures of polyurethanes, which exhibit (a) hydrogen bonded and (b) cross-linking phase-separated urethane blocks [2].

Figure 6.2: Part A: EN4 consists of 10 to 12 parts by weight of free toluenediisocyanate (TDI) and 88 to 90 parts by weight of TDI-terminated polybutadiene (PBD) prepolymer.

Figure 6.3: Part B: EN8 consists of Bis-(2-Hydroxypropyl) Aniline and 2-Ethyl-1,3-Hexane Diol.
6.2 Materials

6.2.1 EN8 Urethane

EN8 urethane was prepared by physically mixing 100 grams of EN4 (Part A, Figure 6.2) with 18.8 grams of EN8 (Part B, Figure 6.3). Of the 100 grams part A, 10 to 12 grams were free toluenediisocyanate (TDI) with the remaining 88 to 90 grams being TDI-terminated polybutadiene (PBD) prepolymer. The diols of Part B (namely Bis-(2-Hydroxypropyl) Aniline and 2-Ethyl-1, 3-Hexane Diol) react with the PBD prepolymer via the isocyanate groups to complete the chain extension. The excess TDI present also reacts with the diols of Part B.

6.2.2 Boron Cage Compounds

Boron cage compounds are a class of icosahedral, closed cage molecules (carboranes -closo-C2B10H12, and dodecaborane anions or boranes -[closo-B12H12]-, Figure 6.4) that are used as nano-fillers to improve the neutron absorbing/shielding property of the composite because the 10B isotope of boron has a high cross-section for neutron capture. BCCs can be highly stable, are non-toxic and chemically modifiable. The particular BCC that is the subject of this study is n-hexylcarborane, shown in Figure 6.5.

6.2.3 Sample preparation

EN8 urethane filled with n-hexylcarborane was prepared by adding n-hexylcarborane to Part A, EN4 described above, and physically mixing with Part B. Films approximately 1.5 mm thick, containing 0 and 5% by weight of n-hexylcarborane, were prepared by degassing for 5 min and then pressing at 110 °C for 30 min. The resulting samples appear clear and pale tan colored. Circular samples with diameter approximately 20.8 mm, suitable for dielectric spectroscopy, were punched from the film. The thickness and standard deviation of the samples was measured at six different points on the sample and the mean and standard deviation of these measurements are listed in Table 6.1.
Figure 6.4: Carboranes -closo-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12}-, and dodecaborane anions or boranes -[closo-B\textsubscript{12}H\textsubscript{12}]\textsuperscript{2-}.

Figure 6.5: n-hexylcarborane.
Table 6.1: Thickness of EN8/n-hexylcarborane samples. ‘EN8/5n-hex’ refers to 5% n-hexylcarborane by weight, etc.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN8/0n-hex</td>
<td>1.575 ± 0.005</td>
</tr>
<tr>
<td>EN8/5n-hex</td>
<td>1.573 ± 0.008</td>
</tr>
</tbody>
</table>

6.3 Experiment

6.3.1 Rheology

The glass transition temperatures of the samples were first determined by rheological measurements. The polymer can undergo a significant change in mechanical strength as the temperature is increased to around \( T_g \), which indicates a transition from rigid to rubbery material. The dynamic mechanical thermal analysis (DMTA) measurement can be conducted on a rheometer (TA Instruments). How a material responds to a dynamic stress depends on its own viscoelasticity. Viscoelastic properties can be characterized by three variables: storage shear modulus \( G' \), loss shear modulus \( G'' \), and phase angle \[3\].

6.3.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the difference in the amount of heat required to increase the temperature of the sample under test and to increase that of a reference sample is measured as a function of temperature. Here, DSC is conducted to establish the degree of crystallinity of the samples. Melting of a crystalline phase is observed as an endothermic peak in the DSC test. EN8/0n-hex and EN8/5n-hex samples were tested over the temperature range from 30 to 270 °C with a heating/cooling rate of 20 °C/min.

6.3.3 Dielectric Spectroscopy

The complex permittivity of the samples was measured using a Novocontrol dielectric spectrometer with automatic temperature control from -140 to 130 °C with a 5 °C temperature
increment over a frequency range from 0.01 Hz to 1 MHz. Electrodes with 20 mm diameter were used.

6.4 Results

6.4.1 Rheology

The positions of the peak maxima in the loss tangent (\(\tan \delta\)) show that the PBD segments are reinforced by the introduction of n-hexylcarborane into EN8 urethane. On the other hand, the urethane segments are plasticized by the presence of the filler. Determined by rheology, the glass transition temperature of the PBD segment of EN8/0n-hex is around \(-86 ^\circ\mathrm{C}\) and two broad transitions of urethane segments are observed at around 50 °C and 70 °C. With the introduction of n-hexylcarborane into EN8, the glass transition temperature of the urethane component is observed to decrease by between 20 and 40 °C, while \(T_g\) of the PBD segments increases slightly by approximately 10 °C. These results are summarized in Table 6.2.

Table 6.2: Rheologically determined transition temperatures of EN8/0n-hex and EN8/5n-hex.

<table>
<thead>
<tr>
<th>Segment, sample</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane, EN8/0n-hex</td>
<td>(\approx 60)</td>
</tr>
<tr>
<td>Urethane, EN8/5n-hex</td>
<td>20 - 40</td>
</tr>
<tr>
<td>PBD, EN8/0n-hex</td>
<td>(-86)</td>
</tr>
<tr>
<td>PBD, EN8/5n-hex</td>
<td>(\approx -76)</td>
</tr>
</tbody>
</table>

6.4.2 Differential Scanning Calorimetry

The result of the first DSC heating test on EN8/0n-hex and EN8/5n-hex is shown in Figures 6.6 and 6.7, respectively. Exothermic peaks occurring between 175 and 185 °C are observed. The precise temperature dependent behavior can be attributed to a chemical reaction taking place in the samples. This observation is probably due to a reaction between unreacted raw materials remaining in the samples after processing. The endothermic peaks appearing at approximately 60 °C in Figures 6.6 and 6.7 are attributed to melting of the regularity formed by diol units in the samples. The exothermic peaks observed between 175 and 185 °C occur in
the same temperature range in which an endothermic peak is expected if there is crystallinity in the PU segments. From these first DSC heating tests, therefore, it cannot be concluded whether or not crystallinity exists in the samples. For this reason, DSC cooling tests were conducted on samples directly following the first heating test. If a certain degree of crystallinity indeed exists in the samples, then exothermic peaks should be visible on cooling, indicating the formation of the crystalline phase. In Figures 6.8 and 6.9 it can be seen that the DSC cooling curve is featureless, indicating that no crystallization process occurs during cooling. Hence we conclude that EN8/0n-hex and EN8/5n-hex are amorphous.

6.4.3 Dielectric Spectroscopy

The imaginary permittivity of EN8/0n-hex and EN8/5n-hex measured as a function of frequency and temperature is plotted in Figures 6.10 and 6.11, respectively. Figures 6.12 and 6.13 show data extracted from the data set shown in Figures 6.10 and 6.11, namely the real and imaginary parts of permittivity of the samples as a function of temperature at various frequencies. Due to the fact that the glass transitions ($T_g$) for EN8 occur from approximately -85 to -40 °C for the soft segment and -20 to 105 °C for the hard segment, it is reasonable to assign the peaks of imaginary part of permittivity at lower temperature to be the $\alpha$ relaxation of PBD and the peaks at higher temperature to be the $\alpha$ relaxation of PU. The dielectric spectra are now modeled in order to extract characteristics of individual relaxations and understand how these are affected by the presence of n-hexylcarborane. In particular, the affect of the presence of n-hexylcarborane on the segmental motions of PU, PBD and polar side groups will be elucidated.

6.5 Modeling the Dielectric Spectrum

In order to extract more precise information about the observed relaxations and their associated molecular dynamics, the $\alpha$-type glass transitions, a secondary $\beta$-type relaxation process and a conductivity term in the dielectric spectrum are modeled by the parametric Havriliak-Negami approach [4]. The dielectric spectrum is decomposed as the sum of four
Figure 6.6: Heat flow measured as sample ENS/0n-hex is heated at 20 °C/min.
Figure 6.7: As in Figure 6.6 but for EN8/5n-hex.
Figure 6.8: Heat flow measured as sample EN8/0n-hex is cooled at 20 °C/min.
Figure 6.9: As in Figure 6.8 but for EN8/5n-hex.
Figure 6.10: Imaginary permittivity of EN8/0n-hex as a function of frequency and temperature.

Figure 6.11: As shown in Figure 6.10 but for EN8/5n-hex.
Figure 6.12: Real and imaginary permittivity of EN8/0n-hex as a function of temperature at 113 Hz and 1.20 kHz.

Figure 6.13: As shown in Figure 6.5 but for EN8/5n-hex.
relaxations and a conductivity term, as described by equation (6.1), and the best fit between experimental data and the model is obtained by least squares regression [5, 6].

\[
\varepsilon^*(\omega) - \varepsilon_\infty = \sum_{p=1}^{4} \frac{\Delta \varepsilon_p}{1 + (i\omega \tau_{p,HN})^{1-\alpha_{p,HN}\beta_{p,HN}}} - \frac{i\sigma}{\varepsilon_0\omega^A} \tag{6.1}
\]

In (1), \(\omega\) is angular frequency, \(p = 1, ..., 4\) denotes the different relaxation types, \(\Delta \varepsilon\) is the dielectric strength, \(\varepsilon_\infty\) is the permittivity well above the frequency of the measurement, \(\sigma\) is the conductivity, \(\varepsilon_0\) is the permittivity of free space, and \(\tau_{HN}, \alpha_{HN}\) and \(\beta_{HN}\) are characteristic relaxation time and shape parameters that describe the Havriliak-Negami function [4]. The term containing the power \(A\) is due to conductivity and electrode effects. \(A\) is always smaller than 1. It is common to proceed by fitting the imaginary part of the permittivity, \(\varepsilon''(\omega)\). By using the least squares fitting techniques, the fitting parameters then satisfy the following criterion:

\[
\sum_{i} \left\{ (\varepsilon''_{\text{exp}})_i + \frac{\sigma_{DC}}{\varepsilon_0\omega_i^A} - \sum_{p=1}^{2} \varepsilon''_{p,HN}(\omega_i) \right\}^2 \rightarrow \text{min} \tag{6.2}
\]

where the sum is over the \(i\) experimental data points and

\[
\varepsilon''_{p,HN}(\omega_i) = \text{Im}\left\{ \frac{\Delta \varepsilon_p}{1 + (i\omega \tau_{p,HN})^{1-\alpha_{p,HN}\beta_{p,HN}}} \right\}.
\]

Above the glass transition temperature \(T_g\), the glassy state is transformed to a rubbery state, also known as a super cooled liquid. The segmental motions and chain connectivity of polymers both contribute to the dynamic glass transition by intramolecular and intermolecular cooperativity. The characteristic relaxation rate of the \(\alpha\) relaxation, which describes the viscosity and structural relaxation, obeys the Vogel-Fucher-Tammann (VFT) law [7][8][9]

\[
f_{\alpha \text{max}} = f_0 \exp \left( -\frac{DT_0}{T - T_0} \right) \tag{6.3}
\]

in which \(D\) is the strength parameter and the temperature \(T_0\) is characteristic of static dipolar freezing of dipolar motion in the absence of long-range correlation.

The fragility of polymers, with index \(m\) [10], is related to the curvature in the plot of \(\log_{10}(f_{\text{max}})\) versus \(1/T\), and is given by
The fragility index $m$ of the sample can be described by the following formula \cite{10} in terms of VFT parameters,

$$m = \frac{T_g}{\ln(10)} \frac{DT_0}{(T_g - T_0)^2}$$  \hspace{1cm} (6.5)

The dielectric $\beta$ relaxation process of amorphous polymers arises from localized rotational fluctuations of side chains. The mechanisms of the $\beta$ relaxation were discussed by Goldstein and Johari \cite{11, 12} who argued that the $\beta$ relaxation universally exists in a great variety of amorphous polymers. The temperature dependence of the characteristic relaxation time of the $\beta$ relaxation follows the Arrhenius law,

$$f_{\beta,max} = f_0 \exp\left(-\frac{E_A}{k_B T}\right)$$  \hspace{1cm} (6.6)

where the factor $f_0$ is on the order of the vibrational frequency of the localized motions, $E_A$ is the activation energy of the $\beta$ relaxation, and $k_B$ is the Boltzmann constant. The relation between maximum relaxation time and the corresponding Havriliak-Negami parameters $\alpha_{HN}$ and $\beta_{HN}$ in Equation (6.1) are \cite{10}

$$f_{\alpha,\beta,max} = f_{HN}^{\alpha,\beta} \left\{ \frac{\sin \left(\frac{\pi(1-\alpha_{HN})\beta_{HN}}{2(\beta_{HN}+1)}\right)}{\sin \left(\frac{\pi(1-\alpha_{HN})\beta_{HN}}{2(\beta_{HN}+1)}\right)} \right\}^{-1/(1-\alpha)}$$

$$f_{HN}^{\alpha,\beta} = 1/(2\pi \tau_{HN}^{\alpha,\beta})$$  \hspace{1cm} (6.7)

where $f_{HN}^{\alpha,\beta} = 1/(2\pi \tau_{HN}^{\alpha,\beta})$ is the characteristic frequency of the $\alpha$ and $\beta$ relaxations. In Fig. 5, the Arrhenius diagram of $\alpha$ and $\beta$ relaxation processes of the investigated samples is plotted. To show an example of the fit of the model to the data, isothermal plots, at $60 \, ^\circ$C, of imaginary relative permittivity are shown for EN8/0n-hex and EN8/5n-hex samples in Figures 6.14 and 6.15, respectively, in which $\alpha$ and $\beta$ relaxation processes and a conductivity terms are identified. The superposed relaxations and conductivity term agree well with the experimental data, where the standard errors of modeling results are 0.0016 and 0.526 for EN8/0n-hex and EN8/5n-hex, respectively. Isothermal data sets were modeled at other temperatures with similar standard errors.
Figure 6.14: Imaginary relative permittivity, $\varepsilon''_r$, of EN8/0n-hex at 60 °C, plotted as a function of frequency.

Figure 6.15: As in Figure 6.14 but for EN8/5n-hex.
The frequency-dependent imaginary permittivity data was modeled in this way at all temperatures from -140 to 130 °C with a 5 °C temperature increment. The relaxation behavior of the two samples is compared in the Arrhenius diagram plotted in Figure 6.16. Shown in Figure 6.16 are the $\alpha$ and $\beta$ relaxations of the PBD and PU segments in EN8/0n-hex and EN8/5n-hex. The fitted parameters of the $\alpha$ and $\beta$ relaxations according to equations (6.3) to (6.6) are listed in Tables 6.3 and 6.4.

Table 6.3: Fitted parameters of the temperature dependence of the $\alpha$ relaxation processes of EN8/0n-hex and EN8/5n-hex, according to equations (6.3) to (6.5).

<table>
<thead>
<tr>
<th>Segment, sample</th>
<th>$f_0$(Hz)</th>
<th>D</th>
<th>$T_0$(°C)</th>
<th>$T_g$(°C)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane, EN8/0n-hex</td>
<td>$9.15 \times 10^6$</td>
<td>2.17</td>
<td>293.8</td>
<td>49.3</td>
<td>111±6</td>
</tr>
<tr>
<td>Urethane, EN8/5n-hex</td>
<td>$1.74 \times 10^8$</td>
<td>3.39</td>
<td>276.7</td>
<td>40.6</td>
<td>94±5</td>
</tr>
<tr>
<td>PBD, EN8/0n-hex</td>
<td>$1.43 \times 10^4$</td>
<td>1.42</td>
<td>178.3</td>
<td>-78.9</td>
<td>85±4</td>
</tr>
<tr>
<td>PBD, EN8/5n-hex</td>
<td>$4.36 \times 10^7$</td>
<td>3.14</td>
<td>176.1</td>
<td>-73.8</td>
<td>90±5</td>
</tr>
</tbody>
</table>

Table 6.4: Fitted parameters of the temperature dependence of the $\beta$ relaxation processes of EN8/0n-hex and EN8/5n-hex, according to equation (6.6).

<table>
<thead>
<tr>
<th>Segment, sample</th>
<th>$A$</th>
<th>$E_A$(KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane, EN8/0n-hex</td>
<td>$4.19 \times 10^{21}$</td>
<td>118±6</td>
</tr>
<tr>
<td>Urethane, EN8/5n-hex</td>
<td>$2.63 \times 10^{20}$</td>
<td>107±5</td>
</tr>
<tr>
<td>PBD, EN8/0n-hex</td>
<td>$2.03 \times 10^7$</td>
<td>11±0.6</td>
</tr>
<tr>
<td>PBD, EN8/5n-hex</td>
<td>$5.49 \times 10^6$</td>
<td>11±0.6</td>
</tr>
</tbody>
</table>

6.6 Discussion

The molecular dynamics of EN8 change significantly when n-hexylcarborane is introduced. As shown in Tables 6.2 and 6.3, the glass transition temperature $T_g$ of the PBD segments increases with the introduction of n-hexylcarborane, while that of the urethane segments decreases. In other words, both plasticization and reinforcement of EN8 occur on addition of n-hexylcarborane. The absence of any crystalline phase in the samples, as indicated by DSC experiments (Figures 6.6 to 6.9) suggests that the observed relaxation mechanisms do not include interfacial polarization (or Maxwell-Wagner-Sillars) relaxation. Further, since in general
Figure 6.16: Arrhenius diagram for EN8/0n-hex and EN8/5n-hex, where $f_{\text{max}}$ is the characteristic frequency of the maxima that appear in the isothermal plots of $\varepsilon''(\omega)$. The lines plotted in this figure are obtained by polynomial fits to the data points and serve only as a guide to the eye.

Figure 6.17: Schematic diagram showing hypothesized mechanism of reinforcement in EN8 urethane/n-hexylcarborane in which the hard PU component of EN8 swells, stretching the PBD segments and causing an observed increase in $T_g$ of PBD.
the glass transitions for EN8 occur from approximately -85 to -40 °C for the soft segment and -20 to 105 °C for the hard segment [13], the observed α relaxations can be assigned accordingly, and other observed relaxations are attributed to localized motions of sidegroups in the form of β relaxations. One possible mechanism of reinforcement of the PBD segments in EN8/n-hexylcarborane is that the n-hexylcarborane concentrates in the hard segments of the sample, PU, causing them to swell. Swelling of this phase might then cause the PBD segments to stretch, as illustrated in Figure 6.17, resulting in restricted motion of the PBD segments and accounting for increase in $T_g$ of PBD. This hypothesis can be confirmed or refuted by determining whether or not the n-hexylcarborane preferentially locates within the PU segment of EN8/n-hexylcarborane.

Consider the fitted parameters of the temperature dependence of the α-relaxation processes of the samples, Table 6.3. As well as reduction of $T_g$ of the PU segment on introduction of n-hexylcarborane to EN8, a reduction in the fragility index $m$ is also observed. Similarly, the increase in $T_g$ observed for the PBD segment is accompanied by an increase in $m$ for PBD. Typically, in a composite, the fragility depends on the particle-polymer interactions and $m$ is expected to increase or decrease due to attractive or repulsive particle-polymer interactions, respectively. The reduction in $m$ for PU therefore indicates the presence of repulsive particle-polymer interactions for the PU segment and, conversely, the increase in $m$ for PBD indicates the presence of attractive particle-polymer interactions. In reference [14], the authors report on the primary association of TiO$_2$ nanoparticles with N-H groups in PU hard segments leading to an increase in the amount of soft domains with high segmental mobility. In that case, lower $T_g$ and $m$ were observed. The observation here, that $T_g$ and $m$ of the PU segments are reduced on introduction of n-hexylcarborane into EN8, may be explained by the same attraction between the nanoparticles, here n-hexylcarborane, and N-H groups in PU. This supports the hypothesis presented above, that the n-hexylcarborane locates preferentially within the hard PU segment of EN8.

Consider the β relaxations of the PBD segments of the two samples shown in Figure 6.16. It can be seen that the β relaxation frequency of the PBD segment of EN8/0n-hex is higher than
that of EN8/5n-hex. This means that the localized motion of dipolar polyether side groups in
the PBD segments of EN8/0n-hex are faster than those of the EN8/5n-hex sample. Conversely,
in the hard PU segments, the $\beta$ relaxation frequency of the PU segment of EN8/5n-hex is higher
than that of EN8/0n-hex. This means that the localized motion of ester complexes [15] in the
PU segments of EN8/5n-hex are faster than those of the EN8/0n-hex sample. Together, these
observations indicate that the introduction of n-hexylcarborane into EN8 produces greater
freedom of motion of the localized alkyl side groups in PU but restricts the motion of the
polyether side groups in PBD.

6.7 Conclusion

The dielectric spectrum of EN8 segmented polyurethanes with 0 and 5% n-hexylcarborane
by weight are investigated by broadband dielectric spectroscopy and parametric modelings.
By comparing the modeling results of fitting parameters, glass transition temperature, and
fragility index, it is observed that reduced localized motion and plasticization of soft PBD
segments, as well as reinforcement of hard urethane segments, occur with the introduction of
the n-hexylcarborane. The n-hexylcarborane added to EN8 polyurethane preferentially locates
within the hard urethane segments of the PU matrix due to favorable interactions with the
N-H groups of those segments. It causes the hard urethane segments of EN8 to swell due to
repulsive particle-polymer interactions, which in turn decreases their fragility index and glass
transition temperature.
References


CHAPTER 7. Conclusion

The motivation of the research work presented in this thesis is driven by the demand of desirable and controllable electromagnetic performance of composites for applications in certain frequency range. The composites studied in this thesis fall in two categories of composites, metamaterials and nanocomposites.

Chapters 2 and 3 of the thesis studied two critical factors in the design of metamaterials for electromagnetic applications, which are the effect of losses and optical bandwidth, respectively. The analytic formulas are derived based on Mie theory and effective medium theory, which can be used to provide guidance for the design of metamaterials. Subsequently, Chapter 4 studied the composite system consisting of coated particles. An explicit analytic formula is successfully derived by the method of Hertz potential expansions under the effective medium regime and the dipole approximation, which can also be used for practical guidance for the design of composite systems for specific electromagnetic applications.

The second part of the thesis focuses on the dielectric study of polymer systems by using the parametric Havriliak-Negami model to interpret experimental data measured by broadband dielectric spectroscopy. Chapter 5 presents a dielectric analysis of poly(methyl methacrylate) (PMMA) and polystyrene-\textit{b}-poly-(methyl methacrylate) (PS-\textit{b}-PMMA) diblock copolymers and PS/PMMA blends in terms of their characteristic relaxation time, fragility index, activation energy, and relaxation strength. In Chapter 6, the effect of the n-hexylcarborane content on plasticization of polybutadiene segments and reinforcement of urethane segments in EN8 urethane are elucidated by a similar type of parametric modelings of the experimentally measured dielectric relaxations.
7.1 Metamaterials

Metamaterials, which are those artificially fabricated to exhibit extraordinary electromagnetic properties, are of great interest to the scientific community due to their desirable microwave and optical applications.

In Chapter 2, an analytic expression for the threshold dielectric loss angle of spherical inclusions, above which DNG behavior is extinguished, is derived by using the Möbius transformation and the dipole approximation of Mies theory. A case study is conducted with a composite system consisting of magnetodielectric particles of which relative permittivity and permeability both are 50 and the volume fraction \( f = 0.5 \). The threshold value of loss tolerance of particles are calculated as \( \tan \delta_{th} = 0.046 \) based on derived formula.

For the perspective of optimal design of metamaterials, the optimization of the bandwidth in specific frequency range is desirable in many cases. In Chapter 3, the percentage bandwidth in which permittivity and permeability of a simple-cubic lattice of identical, magnetodielectric spheres are simultaneously negative, is analyzed based on Mie scattering theory and effective medium theory. It is shown in Chapter 3 that the maximum achievable DNG bandwidth for a simple cubic lattice of spheres with particle volume fraction \( f = 0.3 \) is 7.4\%, when the particle permittivity and permeability are both approximately 14 times greater than those of the matrix.

In Chapter 4, an explicit analytic expression for the effective permittivity or permeability of a simple-cubic array of coated spheres in a matrix is derived by the method of Hertz potential expansions under the effective medium regime and the dipole approximation. A case study of the composite consisting of LiTaO\(_3\) particles coated with doped silicon and embedded in a polystyrene foam matrix for volume fraction \( f = 0.5 \) is conducted, which exhibits maximum possible double negative (DNG) bandwidth of 0.37 THz for shell radius \( a = 3.25 \mu m \) and core/shell radius ratio \( b/a = 0.635 \).

Recent progress in design of non-metallic DNG metamaterials mainly emphasized theoretical developments, such as two or more periodic arrays of magnetodielectric spheres, different types of inclusions and different types of periodic arrangements of inclusions. Because high
values of particle permittivity or permeability are needed, along with tight tolerance of losses and aperiodicity, it is relatively difficult to fabrication of this kind of composite systems. With the recent developments in self-assembly of polymer-matrix systems and nanocomposites with hierarchically ordered structures, it is becoming feasible to fabricate ordered structures of magnetodielectric particles embedded in the polymer matrix. For this reason, the remainder of the thesis is concerned with characterization of the molecular dynamics of block-copolymers that can be utilized in hierarchical ordering, and of nanocomposites.

7.2 Nanocomposites

Nanocomposites, which often consist of a polymer matrix and nanoparticle inclusions, can offer much better mechanical or dielectric performance than individual non-hybrid components and may be tailored to meet different requirements of potential applications.

A dielectric study of PS-b-PMMA diblock copolymers and PS/PMMA are conducted in Chapter 5. Experimental data is obtained by broadband dielectric spectroscopy from 0.01 Hz to 1 MHz over a temperature range of -40 to 150 °C. By parametric fitting techniques based on the Havriliak-Negami model, α-type and β-type relaxations are successfully identified. Values of fragility index, activation energies, and relaxation strength of PMMA and PS-b-PMMA diblock copolymers were compared. Changes of molecular dynamics of samples are also discussed in terms of the dielectric strength on the basis of the Onsager-Kirkwood-Fröhlich theory. It is observed that the structural α relaxation of the copolymers is suppressed compared with other samples.

In Chapter 6, the effect of the n-hexylcarborane content on reinforcement and plasticization of the polyurethane (PU) and polybutadiene (PBD) segments of PU/PBD segmented copolymers are investigated by the method of broadband dielectric spectroscopy and parametric modeling. Two questions are answered by the dielectric study presented in this work. One is the location of n-hexylcarborane content and the other is whether or not localized motions of PBD segments are slowed down. Based on modeling results that fragility index and glass transition temperature of the hard urethane segments decreases, it is observed that
the n-hexylcarborane content preferentially locates within the hard urethane segments. It is also deduced that localized motions of PBD segments are slowed down as observed from the $\beta$–type relaxation processes.

In future, block copolymers can be used to control the spatial distribution of nanoparticles within the target block of copolymers, and provide a controllable method to design long-range ordered magneto-dielectric nanostructures, while ordered structures can be utilized to manipulate electromagnetic properties for potential application in novel devices. The choices of nanoparticles used as inclusions of nanocomposites are ferroelectric materials, such as lead titanate PbTiO$_3$ and barium titanate BaTiO$_3$ because of their high dielectric constants, relatively low dielectric loss and the ability to switch polarization direction, and super paramagnetic iron oxide nanoparticles, e.g., $\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$, which are widely used for data storage and medical applications. Eventually, long-range order structured films or bulk materials may be fabricated via the mixture of nanoparticles and polymers that exhibit ordering.

The contribution of this thesis has been to provide accessible analytical formulas that can be employed to optimize, design or investigate composites in terms of their electromagnetic performance or dielectric properties. My contribution in the field of metamaterials lies in the study of a simple cubic system of identical homogeneous spheres or coated spheres embedded in a matrix, which can be utilized to manipulate electromagnetic properties for potential application in novel devices. My contribution in the area of nanocomposites focuses on investigation of molecular dynamics of polymer matrices and nanocomposites by conducting analysis through parametric modeling of their dielectric spectra.