DETERMINATION OF DENSITY AND MOISTURE CONTENT OF WOOD USING TERAHERTZ TIME DOMAIN SPECTROSCOPY

by

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Abstract

Terahertz time-domain spectroscopy was used to simultaneously predict the density and moisture content of four wood species (Aspen, Birch, Hemlock and Fir). Using a fixed value for the dielectric function of water, it was found that moisture content was systematically underestimated at low moisture contents, which results from changes in the dielectric function of water as it goes from free to bound in nature. The variation of the dielectric function of water with moisture content was studied further, and the results show that the dielectric function of water does indeed change with moisture content. The results are a large step forward in our understanding of wood-water interactions at Terahertz frequencies, and therefore useful for applications in wood science.
List of papers

This thesis is the outcome of my M.Sc. studies in the Department of Physics at the University of Northern British Columbia, Prince George, BC, Canada, from September 2012 to August 2014. The work has resulted in two papers and one invited conference presentation as listed below.


Contributions

**Paper I**: I took an active part in sample preparation, data analysis and writing of the manuscript.

**Paper II**: I developed the model, performed simulation work, data analysis, and wrote the manuscript.
# Table of Contents

Abstract .............................................................................................................................................. i  
List of papers ...................................................................................................................................... ii  
Table of contents ............................................................................................................................. iii  
List of figures ................................................................................................................................... v  
Acknowledgments ........................................................................................................................... ix  

1. Introduction ................................................................................................................................1  

2. Background ................................................................................................................................5  
   2.1 THz spectrum ........................................................................................................................... 5  
   2.2 Terahertz time-domain spectroscopy (THz-TDS) .............................................................. 6  
   2.3 Terahertz emission ............................................................................................................... 9  
   2.4 Terahertz detection ............................................................................................................ 12  
   2.5 Effective medium theory ................................................................................................... 14  
   2.6 Wood structure ................................................................................................................. 16  
      2.6.1 Softwoods and hardwood ..................................................................................... 17  
   2.7 Moisture content .............................................................................................................. 21  
   2.8 Density ............................................................................................................................. 22  
   2.9 Applications of THz technology ...................................................................................... 23  

III
2.9.1 Using terahertz radiation to probe wood .............................................................. 25
2.9.2 Analysis of THz data ............................................................................................ 26
2.9.3 The inverse electromagnetic problem ................................................................. 28

3. Simultaneous prediction of density and moisture content of wood by terahertz time
domain spectroscopy
3.1 Abstract ..................................................................................................................... 32
3.2 Introduction .................................................................................................................. 33
3.3 Materials and methods ............................................................................................... 35
   3.3.1 Sample preparation ............................................................................................. 35
   3.3.2 THz spectral measurement ................................................................................. 37
3.4 Results and discussion ............................................................................................... 37
3.5 Conclusion .................................................................................................................. 54

4. Investigation of the water absorption in wood by terahertz time-domain spectroscopy
4.1 Abstract ..................................................................................................................... 56
4.2 Introduction .................................................................................................................. 57
4.3 Materials and methods ............................................................................................... 60
   4.3.1 Sample preparation ............................................................................................. 60
   4.3.2 THz spectral measurement ................................................................................. 61
4.4 Results and discussion ............................................................................................... 62
4.5 Conclusion .................................................................................................................. 74

5. Conclusion .................................................................................................................... 76
List of Figures

2.1 Electromagnetic Spectrum .................................................................................................... 6

2.2 THz waveform with and without 1mm thick Aspen. The samples have dimensions of 30 mm × 30 mm at a moisture content of 28% ................................................................. 7

2.3 Experimental arrangement for THz-TDS spectroscopy measurements. A THz pulse is obtained when focusing the pump beam onto the photoconductive emitter. The probe beam gates the photoconductive detector co-incident with the THz pulse. By changing the optical delay between probe and THz pulses, the time evolution of the THz pulse is obtained ............................................................................................................................... 9

2.4 Photoconductive THz transmitter. The pump beam illuminates the biased antenna with photon energies greater than the band gap. THz radiation is then radiated from the resulting transient photocurrent according to Maxwell's equations with wavelengths in the terahertz range ........................................................................................................... 11

2.5 Photoconductive THz receiver. The probe beam gates the photoconductive detector by creating a transient conductivity window ........................................................................ 13

2.6 Softwoods: internal structure .............................................................................................. 18

2.7 Hardwoods: internal structure ............................................................................................ 19

2.8 Softwood (left) and hardwood (middle, right) cell wall structure ..................................... 20

2.9 Free and bound water inside wood ...................................................................................... 22

2.10 THz transmission spectroscopy ........................................................................................... 26
2.11 Fabry-Perot reflections ....................................................................................................... 29

3.1 Dependence of moisture content (oven-dry basis) on the variation in relative humidity for maple (open circle), aspen (filled circle), birch (open square) and Western hemlock (filled square) ................................................................................................................................38

3.2 Frequency-resolved (a) real part and (b) imaginary part of the dielectric function obtained from THz transmission spectroscopy of oven-dry wood. Relation between oven-dry density and (c) real part and (d) imaginary part of dielectric function averaged over the frequency range of 0.1 to 0.2 THz (polarization of the THz field is perpendicular to the grain of the wood samples) .......................................................................................................................... 39

3.3 Frequency-resolved (a) real part and (b) imaginary part of the dielectric function obtained in transmission spectroscopy of Birch at various moisture content. Relation between moisture content and (c) real part and (d) imaginary part of dielectric function averaged over the frequency range of 0.1 to 0.2 THz (polarization of THz field is perpendicular to grain of wood) ........................................................................................................................................ 40

3.4 Composite Cylinder Assemblage (CCA) scheme where a cylindrical inclusion of dielectric constant \( \varepsilon_1 \) is surrounded by a cylindrical shell of dielectric constant \( \varepsilon_2 \) leading to a bulk effective dielectric function \( \varepsilon_{\text{eff}} \) .............................................................................................................................. 42

3.5 Effective medium theory applied to determine the bulk effective dielectric function of wood at different moisture contents. The dry cell wall material with dielectric constant \( \varepsilon_{\text{ovenCW}} \) (which is known from measurement – see text for details) is combined with a random distribution of water assumed to have a dielectric function \( \varepsilon_{\text{water}} \) (see text for details) using the Bruggeman model to determine the effective dielectric constant of the wet cell wall material. The MG model with cylindrical symmetry is then applied to combine air, with a dielectric function \( \varepsilon_{\text{air}} \), and the wet cell wall material to determine the effective dielectric constant of the wood, \( \varepsilon_{\text{wetwood}} \) .............................................................................................................................. 46

3.6 Typical set of reference (dot line) and sample (solid line) waveforms along with the best-fit predicted waveform (dashed line) according to the model ........................................................................................................... 50
3.7 Relationship between measured and predicted density based on MG-EMT model. $r^2$, determination coefficient; RMSE, root mean square error. (a) Perpendicular and (b) parallel refer to the polarization of the THz field with respect to the grain of the wood samples ............................................................................................................................... 52

3.8 Relationship between measured and predicted moisture content based on MG-EMT model. $r^2$, determination coefficient; RMSE, root mean square error. Perpendicular and parallel refer to the polarization of the THz field with respect to the grain of the wood samples ............................................................................................................................... 53

4.1 Dependence of the THz field amplitude on the variation of MC in wood. These data are taken at MC between 0% and 30% ............................................................................................................................... 63

4.2 Real part of the dielectric function between 0.2 and 0.5 THz obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir, for the parallel orientation of the wood grain with respect to THz field polarization at MC between 0% and 30% ............................................................................................................................... 64

4.3 Imaginary part of the dielectric function between 0.2 and 0.5 THz obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir, for the parallel orientation of the wood grain with respect to THz field polarization at MC between 0% and 30% ............................................................................................................................... 65

4.4 Real part of the dielectric function of wood obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz ............................................................................................................................... 66

4.5 Imaginary part of the dielectric function of wood obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz ............................................................................................................................... 67
4.6 The real part of the dielectric constant of water at MCs from 1% to 29% for the four wood species: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The upper thick line represents the real part of the dielectric constant of free water and the lower thick line represents the real part of the dielectric constant of ice as per references [68, 69] respectively ................................................................. 69

4.7 The imaginary part of the dielectric constant of water at MCs from 1% to 29% for the four wood species: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The upper thick line represents the imaginary part of the dielectric constant of free water and the lower thick line represents the imaginary part of the dielectric constant of ice as per [68, 69] references respectively ........................................................................................................ 70

4.8 Real part of the dielectric function of water obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz ................................................................................................................ 73

4.9 Imaginary part of the dielectric function of water obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz ........................................................................................................ 74
Acknowledgments

"If the facts don't fit the theory, change the facts" ~Albert Einstein

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Chapter 1

Introduction

Terahertz (THz) radiation lies in the far infrared portion of the electromagnetic spectrum. The possibility for sub-mm imaging capabilities together with the possibility for collecting spectroscopic information, makes this part of the electromagnetic spectrum very attractive for many applications and offers unique capabilities that can be applied to non-destructive testing of materials. The most useful frequency range for applications in wood science fall below about 1 THz [1] with sub-millimeter spatial resolution that is not possible at lower frequencies such as microwave frequencies. Most non-conductive dry materials are transparent in the far infrared spectral region and many materials have ‘terahertz fingerprints’, permitting them to be identified, analysed and imaged. The non-ionizing properties of terahertz radiation and the extremely low power levels typically used make it a safe technology in comparison to X-rays for example. Additionally, THz radiation is sensitive to the internal fibre structure of wood and wood composites [2]. Transparency, good spatial resolution, safety of the radiation and sensitivity to fiber structure make THz radiation an ideal technology to explore for new applications in the wood products industry. In the past two decades, THz science and
technology has shown great potential, and many applications have been identified. THz radiation shows a wide range of applications in the field of physical chemistry, spectroscopy of pharmaceuticals and explosives [3], and medical technology [4]. With respect to the wood science field, THz radiation can be used to map density profiles of wood in transmission with sub-annual ring resolution [5]. This transmission imaging is at exactly the spatial length scale important for wood science, and subsequently has led to applications in dendrochronology [6].

There are different techniques that have been developed for studying the density of wood with sub-annual ring resolution. These techniques are classified into, mechanical and spectroscopic methods. The hardness feeler is one of the mechanical methods that was used to study the density of wood, and uses a pin which is pressed into the wood at a defined pressure [7]. The acid-corrosion method is one in which wood is burned by sulfuric acid and subsequently scrutinized with an optical microscope [8]. In gravimetric-volumetric methods wood is cut into slices and weighed and the volume is subsequently determined [9]. Laser-sandblasting has been used to study hardness profiles, and is implemented by sandblasting wood specimens [10]. The common disadvantage of these mechanical methods is that they damage the sample under study, and hence are destructive methods.

Many ranges of the electromagnetic spectrum have been used to study wood properties. The electromagnetic spectrum is usually classified in terms of wavelength, frequency, or energy. It includes radiowaves, microwaves, THz or far-infrared, infrared, visible light, ultraviolet, X-rays, and γ-rays in order of increasing frequency. Wood is opaque in the ultraviolet, visible and infrared and imaging is therefore limited to reflection geometries [11]. In contrast, wood is transparent at X-ray [12] and microwave [13] frequencies and measurements can be obtained in a transmission geometry. Both microwave and X-ray methods are useful for defect scanning and
quality control and are currently used in the wood products industry. The ultimate spatial resolution possible depends on the radiation wavelength, which means that sub-annual ring resolution cannot be achieved with GHz frequency microwaves (~cm wavelengths). X-rays can be used to get good spatial resolution; however, safety regulations need to be in place because they are dangerous. For these reasons, it is useful to introduce new imaging techniques that have good spatial resolution, are non-destructive, and safe to work with.

In this thesis, THz spectroscopy was used to perform transmission measurements in the far-infrared range of the electromagnetic spectrum. The high sensitivity of THz radiation to moisture content (MC) [14] offers the possibility for probing MC as well. Simultaneous measurement of MC and density has only been demonstrated in a lab environment, using microwave sensors. Although, there are limitations using these sensors such as the high noise in amplitude and the restriction to one period for phase measurements [15], they remain important to the wood products industry. It is therefore of interest to look at new techniques to simultaneously measure MC and density; this problem is the subject of this thesis.

In order to simultaneously determine the wood density and MC, a number of systematic studies were performed in this thesis. Before introducing these studies, background concepts are presented in Chapter 2.

In Chapter 3, wood-water interactions are investigated using THz technology, which is necessary to understand how moisture content affects the properties of wood at THz frequencies. This is achieved by modeling the interaction of THz radiation with wood at different MC's and comparing the model to experiments. In this experiment, four different wood species were
conditioned at different MC's. Density and MC effects of THz radiation interactions in wood were studied using an effective medium theory (EMT).

In Chapter 4, the effect of MC on the dielectric function of water is studied to complete the theoretical model developed in Ch.3. THz spectroscopy enables the investigation of water dynamics due to its sensitivity to dielectric relaxation processes associated with water molecular reorientation. The results show moisture content to be the major influencing factor for the variation of dielectric properties of hydrated wood. As moisture content decreases, it is shown that the dielectric function of wood decreases. A model for the dielectric function of water in wood is developed, which allows us to study changes with moisture content as the water changes from bound to free in form. This model for the dielectric function of water significantly advances our understanding of THz-wood interactions.
Chapter 2

Background

2.1 THz Spectrum

The THz region of the electromagnetic spectrum lies in the far-infrared, between microwave and infrared frequencies, (Figure 2.1). THz radiation is loosely defined by frequencies between 0.1 and 10 THz. THz radiation has a submillimeter wavelength which allows a good spatial resolution compared to microwave radiation. THz radiation is non-ionizing and poses no significant health concerns [2] in contrast to X-rays. On the other hand, THz radiation cannot penetrate metals and is strongly absorbed by water, being a polar molecular. Most non-conductive dry materials are transparent at THz frequencies, which allow transmission imaging. THz radiation is also sensitive to the internal fibre structure of wood and wood composites which makes THz radiation of great importance to wood science [16].
2.2 Terahertz Time-Domain Spectroscopy (THz-TDS)

Terahertz transmission spectroscopy can be performed either directly in the time-domain or in the frequency domain by Fourier transformation of the acquired data. The measurement method used in this thesis is terahertz time-domain spectroscopy (THz-TDS) where all the measurement are made in the time domain and the electric field is measured as a function of time, which is possible because of the coherent detection using photoconductive antennas.

In the time domain experiment, absorption results in a decrease of the amplitude and a (possibly frequency-dependent) phase shift of the detected terahertz pulse. A temporal electric field obtained from a THz-TDS spectrometer is shown in Fig. 2.2. The black signal represents
the reference signal where no sample is in place, and the red signal represents the signal that is transmitted through the sample. By comparing the THz waveforms acquired with and without the sample in place the complex permittivity and refractive index of the material under study can be determined.

Fig. 2.2 THz waveform with and without 1mm thick Aspen. The samples have dimensions of 30 mm × 30 mm at a moisture content of 28%.

One of the original THz-TDS experiments was performed in 1989 by van Exter et al. where the propagation of the terahertz pulses through water vapour was studied [19]. While there are many techniques to generate and detect THz radiation, the use of photoconductive antennas
that was reported in [19] was unique in that it employed coherent detection, mapping the THz field directly in time. Most electromagnetic detectors measure the intensity of light and do not resolve electromagnetic fields in time because of the extremely fast variation of the electromagnetic field.

In order to achieve coherent detection, THz-TDS uses an ultrashort laser (on the order of 100 femtosecond) to generate and detect the terahertz pulses. This ultrashort pulse is divided into two parts, one part is used to generate the terahertz pulse and the other is to gate the detector and arrives simultaneously with the terahertz pulse. Once the gate pulse arrives at the detector, a current is generated that is proportional to the electric field of the terahertz pulse (which is the coherent detection). Fig. 2.3 shows the experimental setup for THz-TDS spectroscopy, and the physical mechanism behind generation and detection is discussed next.
2.3 Experimental arrangement for THz-TDS spectroscopy measurements. A THz pulse is obtained when focusing the pump beam onto the photoconductive emitter. The probe beam gates the photoconductive detector co-incident with the THz pulse. By changing the optical delay between probe and THz pulses, the time evolution of the THz pulse is obtained.

2.3 Terahertz emission

Generation and detection of pulsed THz radiation was first demonstrated using photoconductive antennas by Auston et al. in 1984 [17]. There are many methods for generating pulsed THz radiation, including nonlinear optical methods [18], and photoconductive antennas [17, 18]. In this thesis, a photoconductive switch was used to generate and detect THz radiation, and the principles of operation are described next.
Terahertz generation using photoconductive antennas

Figure 2.4 illustrates the mechanism of generation of THz radiation using a photoconductive antenna. An ultrashort femtosecond laser (typically with a pulse width around 100 fs) illuminates a biased antenna on a semiconductor surface with photon energies greater than the band gap, which creates a transient photocurrent. The transient photocurrent $J_{\text{transient}}(t)$ is generated by the acceleration of photocarriers in the bias electric field. Terahertz radiation is then radiated from the transient photocurrent according to Maxwell's equations with wavelengths in the terahertz range [18]. The THz radiated electric field, $E_{\text{THz}}$ is directly proportional to the temporal derivative of the transient photocurrent generated in the transmitting antenna, $\frac{df}{dt}$. A silicon lens is usually attached to the antenna to collimate the THz beam that is generated as shown in Fig. 2.4.
Fig. 2.4 Photoconductive THz transmitter. The pump beam illuminates the biased antenna with photon energies greater than the band gap. THz radiation is then radiated from the resulting transient photocurrent according to Maxwell's equations with wavelengths in the terahertz range.

THz radiation can be generated from a photoconductive antenna using a variety of materials such as gallium arsenide (GaAs) and InGaAs, depending on the optical wavelength used for excitation. Usually, a substrate with a short carrier lifetime in the sub-picosecond range is desirable to maximize the variation of the transient photocurrent, which is why low temperature (LT) GaAs, which has a sub-ps carrier lifetime, is often used instead of GaAs which has a carrier lifetime with several hundred picoseconds [20]. For this reason, low temperature (LT) GaAs substrates are used in our system.
2.4 THz detection

There are two primary methods for the coherent detection of THz radiation: (1) electro-optic sampling and (2) photoconductive sampling. In this work, photoconductive sampling is the method used for THz detection and details about this method and its advantages will be discussed in the next section.

Terahertz detection using photoconductive sampling

Terahertz detection using photoconductive sampling is similar to photoconductive generation except that the bias electric field across the antenna comes from the electric field of the THz pulse focused onto the antenna. A typical H-structured dipole photoconductive antenna is shown in Fig. 2.4. An ultrashort femtosecond laser illuminates the 5 μm gap between the electrodes on the semiconductor surface with photon energies greater than the band gap creating a transient conductivity window. The THz field then drives a current proportional to the THz field over the lifetime of the transient conductivity. This current is amplified and detected with a lock-in amplifier at a frequency equal to the frequency at which the emitter bias is modulated. This amplified current is then a convolution of the THz field and the transient photoconductivity window. Because the window is short in time (sub-ps), the current collected is approximately proportional to the THz field [29, 30],

\[ j(t) = \frac{n(t)e^2}{m}E_{THz}(t). \]  
Eq. 2.1

where \( E_{THz}(t) \) is the field of the incoming THz pulse, \( n(t), q, m \) are the density, charge, and mass of the photocarriers respectively.
Fig. 2.5  Photoconductive THz receiver. The probe beam gates the photoconductive detector by creating a transient conductivity window.

The antenna response function is frequency-dependent, and depends on the coupling of the THz field into the antenna and the impedance matching conditions of the antenna to the transmission line [21]. In this work, TERA8-1 photoconductive antennas made from low temperature (LT) GaAs substrates, were used to generate and detect THz radiation. These antennas can generate THz radiation with a bandwidth up to about 4 THz. A Menlo system with TERA8-1 photoconductive antennas was used to investigate the THz transmission through wood. We also used a modified Picometrix T-Ray 4000 system (discussed later in the thesis), which is also based on photoconductive emitters and detectors.
THz radiation is sensitive to water [32] which makes it a useful tool in predicting moisture content (MC) in wood. The properties of wood (such as density and moisture content) vary significantly within and between the different wood species, which affect structural properties, and therefore dictate performance characteristics. In this work, a new THz-TDS methodology to simultaneously predict density and MC is introduced. The ability to use THz radiation to measure density and moisture content simultaneously is extremely important for the wood products industry. In order to exploit THz technology for moisture content determination, a model for the interaction with THz radiation is required. Wood contains 3 different materials: air, water and cell wall material (cellulose, hemicellulose and lignin). Effective medium theories (EMT) are traditionally used to look at composite systems, and were applied to wood in this thesis to model the THz-wood interaction. The most commonly used EMT's are presented next, and a basic overview of the characteristics of these models is introduced.

2.5 Effective Medium Theory

Maxwell-Garnett Model

The Maxwell-Garnett (MG) model is one of the most well-known EMTs and it is based on analyzing the effective polarizability of spherical inclusions embedded in a host matrix. This model is suitable to low volume fractions of inclusions. The MG model can be derived using basic electrostatics and by knowing the permittivity of the host material [24]. The expression that gives the effective permittivity of the composite system is:

\[
\frac{\varepsilon_R - \varepsilon_h}{\varepsilon_R + 2\varepsilon_h} = f_p \frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p + 2\varepsilon_h}
\]

Eq. 2.2
where $\varepsilon_R$ is the effective permittivity of the composite medium; $\varepsilon_h$ is the permittivity of the host material; $\varepsilon_p$ is the permittivity of inclusions; and $f_p$ is the volume fraction of inclusions. The MG model is not generally used when a large contrast in permittivity between inclusions and host exists [24]. In such cases, other models are usually used to describe the permittivity of composites. One such model is the Bruggeman model [25].

**Bruggeman Model**

The Bruggeman model in its basic form describes spherical particles embedded in a host material, and can be used when a large contrast in permittivity exists. The basic form of the Bruggeman model is given by Eq. 2.3 [25]:

$$1 - f_p = \frac{\varepsilon_p - \varepsilon_R}{\varepsilon_p - \varepsilon_h} \sqrt{\frac{\varepsilon_h}{\varepsilon_R}}, \quad \text{Eq. 2.3}$$

Another more general form can be derived when combining Bruggeman with Polder and van Santen approach. This form is known as the extended Bruggeman (EB) and is a function of the depolarization factor $N$, which is a geometrical factor that accounts for the geometry of the inclusions. The general form of the EB model is given by Eq. 2.4 [26, 27],

$$f_p = 1 - \left(\frac{\varepsilon_h}{\varepsilon_R}\right)^{\frac{-3N^2+3N}{3N+1}} \left(\frac{\varepsilon_p - \varepsilon_R}{\varepsilon_p - \varepsilon_h}\right)^{\frac{12N-18N^2-2}{9N^2-12N-5}}, \quad \text{Eq. 2.4}$$

All of these models are used to describe the effective dielectric properties of mixtures in the THz range but with certain conditions. For example, Maxwell-Garnett theory calculates the effective dielectric properties of a material formed by the presence of small (spherical) particles embedded in a host material [24]. The Bruggeman model is used to calculate the effective
dielectric properties of many components in a mixture [25]. For this reason, it is important to try several effective medium models and then choose the model which best fits the experimental data [25]. In this work, a new model that incorporates a Bruggeman EMT model combined with a Maxwell-Garnet EMT (MG-EMT) is described, and shown to be effective for extracting density and MC from THz measurements for the wet wood. Due to the random distribution of water molecules in the wet wood, a Bruggeman EMT model was used to obtain an effective medium approximation for the hydrated cell wall, while MG EMT model was used to obtain an effective medium approximation for the oven dried cell wall because it can be modified to account for the cylindrical symmetry of the wood system.

As mentioned above, the appropriate effective medium model depends strongly on the internal structure of wood. Wood structure varies between species and in order to use the best EMT model, information about the wood structure should be examined in more details.

### 2.6 Wood structure

Simply, wood is a natural and renewable material, which is widely used in construction, and more and more engineered wood products are continually being developed. Chemically, wood is a porous material consisting mainly of cellulose, hemicelluloses and lignin. Anatomically, the structure of wood is complicated, but in simple terms, the cell wall of wood is a repetitive array of cylindrical pores.

Wood species are classified into two groups: hardwoods and softwoods. Hardwood and softwood trees are botanically different. They are included in the botanical division
spermatophytes, which mean that they produce seeds. Softwoods are in the gymnospermae subdivision and hardwoods are in the angiospermae subdivision [28]. Softwood trees are characterized by needle-like leaves in contrast to hardwood trees which are leaf-bearing. [28].

As shown in Fig. 2.6 and Fig. 2.7, the wood of a hardwood tree is much different than that of a softwood tree. Hardwoods are composed of different types of cells and have more complex anatomical elements in contrast to softwoods which usually have a uniform arrangement with fewer complex cell types. Hardwoods are also normally denser than softwoods. These factors mean that hardwoods will interact in a different way with THz radiation than softwoods. Due to the difference in structure between hardwoods and softwoods, it is necessary to consider both types of species in order to determine how density changes according to their internal structure. The structure of each wood species will be introduced in more details in the next section.

### 2.6.1 Softwoods and Hardwoods

The main difference between softwoods and hardwoods is found in the microscopic structure of wood. Softwood contains two main types of cells: longitudinal wood cells (called tracheids) and transverse ray cells (called parenchyma). The tracheids are responsible for the mechanical support and the water conduction functions in the tree. The parenchyma cells are responsible for nutrients storage. Hardwoods have fiber cells for support and vessel elements for water conduction. The softwood tracheids are about four times longer (approximately 2.5-5 millimeters) and ten times narrower than hardwood vessels. The difference in internal structure of softwoods and hardwoods can be clearly seen in Fig. 2.6 and Fig. 2.7. Another difference between softwoods and hardwoods is that softwood tracheids are closed at each end with tiny
openings called pits, as shown in Fig. 2.8, while hardwood tracheids are open at each end and are free of pits.

Fig. 2.6 Softwoods internal structure [30].
Fig. 2.7 Hardwoods internal structure [30].
Fig. 2.8 Softwood (left) and Hardwood (middle, right) cell wall structure [28].

Since there are different anatomical structures between hardwoods and softwoods, the density is different. This means that their reaction to any variation in the environmental conditions (temperature and humidity) will cause changes in moisture content. For this reason, different wood species from hardwoods and softwoods will be chosen in this work to investigate how their densities change with changing moisture content and if the internal structure has an effect.
2.7 Moisture content

Wood is a hygroscopic material where the MC will change based on the surrounding relative humidity (RH) and temperature (T). Wood swells or shrinks depending on the increase or decrease in its MC. When wood is exposed to constant temperature and humidity, it achieves equilibrium moisture content (EMC). Moisture content in this study is defined as the percentage difference between the wet mass and the oven dried mass:

$$EMC = \left( \frac{m - m_{od}}{m_{od}} \right) \times 100\%,$$

where $m$ is the wet mass and $m_{od}$ is the oven-dry mass [37, 38].

Chemically, wood is composed of hemicelluloses, cellulose, lignin and water. Water in wood is found in two different forms, free water (liquid-like) and bound water. Free water is contained in the cell lumen voids and is held by capillary forces only. Bound water is chemically bound to the cell wall by intermolecular hydrogen bonds with the hydroxyl groups of the cellulose molecule. Fig. 2.9 shows how the two different kinds of water found inside the wood material. When the cell walls are saturated with bound water without any free water found in the cell lumens, the wood is referred to being at the fiber saturation point (FSP).
The presence of bound water in wood softens the cell walls and the hydrogen bonds between cellulose and water are stronger than between cellulose, making hydrogen bonding with water energetically more favourable. Therefore, the cellulose microfibrils are no longer strongly bonded to each other, making it easier to move leading to a decrease in the stiffness of wood [32].

2.8 Density

Wood density is considered an important wood quality attribute. There are several definitions of density including basic density, defined as the weight of oven dry wood at
maximum volume (MC ≥ fibre saturation point) [33]. Generally, density is measured as mass per unit volume [34]:

\[ \rho' = \frac{m}{V}, \]  
Eq. 2.6

where \( \rho' \) is the density, \( m \) is the mass and \( V \) is the volume.

The density of wood is not a fixed value but varies with MC and its mass also changes because the wood swells or shrinks depending on adsorption or desorption. It also varies from species to species. For this reason, the ability to simultaneously predict density and MC is important for the wood industry. To do this, a non-destructive wood inspection tool is highly desirable.

2.9 Applications of THz technology

THz radiation has been studied for a wide range of applications, including applications in security [3], the spectroscopy of pharmaceuticals and explosives [3], medical applications [4] and quality control [14].

Applications of THz radiation are seeing significant interest at the present time. There are many potential uses in the wood products industry for process quality control based on wood properties such as density, grain angles and moisture content. It was determined early on that THz radiation could be used to create a density map of beech wood with sub-annular ring spatial resolution [5]. The prediction of wood density in that work was based on a strong relationship between the absorption coefficient of the wood and the density at THz frequencies [24].
Further studies have recently shown that predicting the oven-dried density of wood using THz-TDS is possible [35]. The results showed a very good correlation over 46 wood species, indicating that THz spectroscopy is applicable to a wide range of very different species. An effective medium theory (EMT) was applied to predict the density from the THz measurements. The Maxwell Garnet (MG) model discussed in section 2.6 was modified for a cylindrical symmetry, and used to describe the THz-wood interaction. This model was based on analyzing the effective polarizability of cylindrical inclusions and was shown to work very well for the case of oven-dried wood [35]:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{cw}}}{\varepsilon_{\text{eff}} + \varepsilon_{\text{cw}}} = f_a \frac{\varepsilon_a -\varepsilon_{\text{cw}}}{\varepsilon_a + \varepsilon_{\text{cw}}},$$  

Eq. 2.7

where $\varepsilon_{\text{eff}}$ is the effective dielectric constant of the cell wall material; $\varepsilon_{\text{cw}}$ is the dielectric constant of the cell wall material; $\varepsilon_a$ is the dielectric constant of air (assumed to be 1); and $f_a$ is the volume fraction of air.

The properties of wood change with changing moisture content and another model capable of incorporating large dielectric contrasts (for including water) is needed when measuring the dielectric constant of the wet cell wall material. Wood naturally contains some moisture, which has an impact on the strength, stiffness, or durability of wood products. The simultaneous measurement of density, gross fiber structure and moisture content makes THz technology an interesting tool for the wood products industry.
2.9.1 Using terahertz radiation to probe wood

THz Measurement configurations

The experimental configuration of a THz-TDS system is usually either in transmission or reflection. A Transmission geometry is highly desirable for applications, and is the geometry used in this work and is discussed in more details in the next sections.

Transmission

In this configuration, the emitter and detector were arranged in a line. A sample holder on a rotation mount was placed in between the transmitter and detector to hold the sample. The sample can be mounted at any angle using this holder. Usually, an aperture or lens is used to narrow the beam so the beam passed only through the sample.

The measurement procedure for the transmission geometry was as follows: (1) a reference scan was taken with no sample is place, (2) a background scan was taken by blocking the holder using a material that is opaque to THz radiation, (3) a scan of the sample was taken to compare to the reference using certain models that will be discussed later. The transmission configuration setup was as shown in Fig. 2.10.
2.9.2 Analysis of THz Data

In this section, the methods of extracting the information from the collected data are discussed in more details.

Phase unwrapping

Phase information is required to calculate the index of refraction and absorption coefficient from the collected THz data. According to Duvillaret et al., the measured signal is very small compared to the noise level at low frequencies [38], which results in a phase that may not go to zero at zero frequency as must physically happen. The distorted phase at the low frequency points is linearly extrapolated [39] to account for this, and implemented in the analysis conducted in the experiments that follow.

Data is collected using transmission geometry. To analyze the data, the Matlab programming language was used to solve for the index of refraction and the absorption coefficient. Two different methods were used to analyze the data: (1) the thick sample approximation of Duvillaret [39], and a purely numerical scheme (the inverse problem) (2) [40].
The complex dielectric function is calculated from the THz measurements by using the thick-sample approximation of Duvillaret [40]:

\[
\frac{E_{\text{wood}}(v)}{E_{\text{ref}}(v)} = \hat{t}_{AW} \hat{t}_{WA} \exp \left[ -\frac{i2\pi v L}{c} (\hat{n}_w - \hat{n}_a) \right],
\]

Eq. 2.8

where \(E_{\text{ref}}(v)\) is the electric field amplitude of the reference spectrum, \(E_{\text{wood}}(v)\) is the electric field amplitude of the transmitted spectrum, \(v\) is the frequency, \(L\) is the thickness of the wood sample under study, \(c\) is the speed of light, \(\hat{n}_w\) is the refractive index of wood, \(\hat{n}_a\) is the refractive index of air, \(\hat{t}_{AW}\) and \(\hat{t}_{WA}\) are the Fresnel transmission coefficients from air to wood and wood to air respectively which can be found for normal incidence as given by:

\[
\hat{t}_{ij} = \frac{2\hat{n}_i}{\hat{n}_i + \hat{n}_j},
\]

Eq. 2.9

where \(\hat{n}_i\) is the index of refraction for the first material, \(\hat{n}_j\) is the index of refraction for the second material. In our case, the two indices will be those of air and wood. The index of air is taken to be 1 and the index of wood is a complex value defined as:

\[
\hat{n}_w = n_w + ik_w,
\]

Eq. 2.10

where \(n_w\) and \(k_w\) are the real and complex index of refraction for wood respectively.

The index of refraction and absorption coefficient of wood is calculated as [36]:

\[
n_w = -\frac{\theta c}{2\pi v L} + 1,
\]

Eq. 2.11

\[
\alpha_w = -\frac{2}{L} \ln \left[ R \frac{(n_w+1)^2}{4n_w} \right],
\]

Eq. 2.12
where $\alpha_w = 4\pi v k_w / c$, $R$ and $\theta$ are the amplitude and phase of the ratio of the reference field to the transmitted field when written in Euler form,

$$\frac{E_{\text{trans}}(\nu)}{E_{\text{ref}}(\nu)} = R e^{i\theta}, \quad \text{Eq. 2.13}$$

where $E_{\text{ref}}(\nu)$ is the reference field in the frequency domain, and $E_{\text{trans}}(\nu)$ is the transmitted field in the frequency domain.

### 2.9.3 The inverse electromagnetic problem

The refractive index can also be measured by measuring the effect caused on the electric field of a THz wave after passing through the material under study as presented in [40]. Assuming $E_{\text{ref}}^{ex}(\omega)$ and $E_{\text{trans}}^{ex}(\omega)$ are the measured reference and sample signals, the frequency dependent transfer function can be written as [40]:

$$H_{\text{experiment}}(\omega) = \frac{E_{\text{trans}}^{ex}(\omega)}{E_{\text{ref}}^{ex}(\omega)}, \quad \text{Eq. 2.14}$$
As shown in Fig. 2.11, the signal propagation through the sample is divided into several stages. First, the incident signal $E_{\text{init}}$ on the front (left) surface of the sample split into two signals, reflected and transmitted [40]. The reflected signal is not a part of $E_{\text{trans}}$ and so will be discarded. The transmitted signal is equal to $E_{\text{init}} t_{01}$ and propagates through the sample [40]. This transmitted signal has an electric field of $E_{\text{init}} t_{01} P_1(l)$ on the second (right) surface of the sample. At this surface, the signal splits again into reflected and transmitted signals [40]. The transmitted portion has an electric field of $E_{\text{init}} t_{01} P_1(l) t_{10}$ and is a part of $E_{\text{trans}}$. This leads to the well-known Fabry-Perot reflections [40]. The THz pulse propagates through air between the two antennas, which is taken into account by the propagation factor $P_0$. After collecting all of the multiple reflections, the overall field can be written as [40]:

$$E_{\text{trans}} = E_{\text{init}} P_0 (x - l) t_{01} P_1(l) t_{10} [1 + \sum_{l=1}^{\delta} (r_{10}^2 P_1^2)^l].$$  

Eq. 2.15
where $\delta$ represents the number of Fabry-Perot reflections, $l$ is the thickness of the sample, $r_{01}$ is the Fresnel reflection coefficient from air to sample, and $t_{01}$ is the Fresnel transmission coefficient from air to sample, which can be calculated using Eq. 2.9. The reference THz field propagates through air only, and is calculated by [40]:

$$E_{\text{ref}} = E_{\text{init}0}(x), \quad \text{Eq. 2.16}$$

Now, the theoretical transfer function can be written as [40]:

$$H_{\text{theo}} = \frac{E_{\text{trans}}}{E_{\text{ref}}} = P_0 (-l) t_{01} P_1 t_{10} \left[ 1 + \sum_{i=1}^{\delta} (r_{10}^2 p_{i}^2) t_{i} \right], \quad \text{Eq. 2.17}$$

The material parameters $n$ and $k$ can be extracted numerically from this transfer function. To do this, a range of values for $n$ and $k$ are assumed, and the values are varied until $H_{\text{theo}}$ is arbitrarily close to $H_{\text{exp}}$. In order to achieve proper convergence, the number of Fabry-Perot reflections must be assumed. This can be done by assuming an initial value for $n$ and $k$ as follows [40]:

$$E_{\text{trans, max}} = E_{\text{ref, max}} \exp \left( -\frac{\omega}{c_0} k_1 l \right), \quad \text{Eq. 2.18}$$

where $E_{\text{trans, max}}$ and $E_{\text{ref, max}}$ represent the maximum field of the transmitted and reference signals respectively.

$$k_1 = -\frac{1}{l} \frac{c_0}{\omega} \log \left| \frac{E_{\text{trans, max}}}{E_{\text{ref, max}}} \right|, \quad \text{Eq. 2.19}$$

$$\Delta t = \frac{i\Delta n}{c_0}, \quad \text{Eq. 2.20}$$

$$n_1 = \frac{c_0 \Delta t}{l} + n_0, \quad \text{Eq. 2.21}$$
where $\Delta t$ is the time delay between the two signals, $l$ is the sample thickness, $c_0$ is the speed of light, and $\Delta n$ is the index difference between wood and air.

Assuming $t_{\text{max}}$ is the maximum time of a measurement since the incidence of the reference signal, which is taken to be the temporal window of data collection. The THz beam propagates along a path of length equal to the sample thickness $l$ with a speed $\frac{c_0}{n_1}$ inside the sample. So, the number of Fabry-Perot reflections $\delta$ is the greatest integer that satisfies the following relation [40]:

$$t_{\text{max}} \geq \frac{n_1}{c_0} l(1 + 2\delta),$$  \hspace{1cm} \text{Eq. 2.22}

This method can then be implemented numerically to extract $n$ and $k$ when the samples are thin and multiple reflections fall within the temporal window of the accumulated THz signals.
Chapter 3

Simultaneous prediction of density and moisture content of wood by terahertz time domain spectroscopy

3.1 Abstract

In this study, demonstration of simultaneous prediction of solid wood density and moisture content, both of which are critical in manufacturing operations, of 4 species (Aspen, Birch, Hemlock and Maple) was accomplished using terahertz time-domain spectroscopy (THz-TDS). THz measurements of wood at various moisture contents were taken for two orientations of the THz field (parallel and perpendicular) with respect to the visible grain. The real and imaginary parts of the dielectric function averaged over the frequency range of 0.1 to 0.2 THz strongly correlate with density and moisture content of the wood. We extend a model

previously applied to oven-dry wood to include the effects of moisture below the fiber saturation point by combining two effective medium models, which allows the dielectric function of water, air and oven-dry cell wall material to be modeled to give an effective dielectric function for the wood. A strong correlation between measured and predicted values for density and moisture content were observed.

3.2 Introduction

Wood is a natural material widely used for its versatility and strength in construction. There are significant variations in the properties of wood (density, moisture content and grain angle for example) within and between species, which affect structural properties, and therefore dictate performance characteristics. When wood is processed industrially, where uniformity of the raw materials is critical for the reliability of the end product, such variations in physical properties must be measured at least, and preferably controlled.

There is a strong relationship between the density of wood and its moisture content, namely, as moisture content increases, density increases. Further, an end-use product such a dimension lumber must have certain strength to meet grading rules criteria for market consumers [41]. To meet the rules, the lumber is tested for its modulus of elasticity, which is based on density [42]. As well as the impact of density, the grading rules also dictate that the moisture content be within a specific range. Measuring both density and moisture content has been done in a laboratory setting, but not on an industrial scale.
The wood cell wall consists of cellulose, hemicellulose, lignin and extractives. The density of cell wall is almost the same for all species of wood (about 1.4 g cm\(^{-3}\)) [43]. However, since the size of the cell and cell wall thickness (the ratio of the cell wall to air) differ between species, the density of wood varies from about 0.1 to 1.2 g cm\(^{-3}\).

Given the above, wood density strongly influences such properties as the modulus of elasticity (MOE) and stiffness, which play a critical role in the manufacturing of wood products. Generally, higher density wood has a higher MOE [42]. Determining the MOE of wood can be done using non-destructive methods such as static bending [42], stress-wave propagation [44], microwave [45] and near infrared [46] with an overall goal of using such techniques for in-line applications.

The dry basis moisture content (MC) of wood is defined as the ratio of water mass in wood to the mass of oven-dry wood. In a living tree, there is free water, which exists in the lumen or free space in the wood, and bound water, which is held in the amorphous region within the cellulose, hemicellulose and on the surface crystalline region of cellulose by hydrogen bonding [32]. When the wood is dried, free water is preferentially evaporated into the atmosphere. Around a MC of 25-30 %, which is known as the fiber saturation point (FSP), all free water is evaporated. The bound water strongly affects the properties of wood, and so control and monitoring of MC during the manufacturing process is important [33].

Terahertz (THz) radiation has the potential to be a useful tool for sensing and imaging of wood because wood is relatively transparent at these frequencies (below about 1 THz), the wavelengths are sub-mm which offers good spatial resolution for imaging, and THz radiation can probe the gross fiber structure of wood. There have been several reports on the interaction of
THz radiation with wood [5, 14, 38, 48-51], which have highlighted applications of THz radiation to the wood products industry, including density mapping [5], defect detection [14], properties of paper [52] and wood-plastic composites [53], dendrochronology [6], and sensitivity to internal moisture suitable for imaging of MC [51].

To date, the prediction accuracy of various species of wood by THz spectroscopy has been demonstrated on oven-dried wood [38], and requires quantification over a range of moisture contents in order to further our understanding of THz-wood interactions so that new applications of this emerging technology related to wood science and the wood industry can be explored further. We showed an excellent correlation between the predicted and measured volume fractions of cell wall material (density) over a large range of volume fractions ($f = 0.2-0.8$), by applying a Maxwell Garnett (MG) effective medium theory (EMT) approach [38]. Here, we show the prediction accuracy is retained over a range of moisture contents below the fiber saturation point, and also demonstrate the possibility for simultaneous extraction of MC and density.

### 3.3 Materials and Methods

#### 3.3.1 Sample preparation

Aspen (*Populus tremuloides*, $\rho_{\text{ovenwood}} \approx 0.49 \text{ g cm}^{-3}$), birch (*Betula spp*, $\rho_{\text{ovenwood}} \approx 0.64 \text{ g cm}^{-3}$), Western hemlock (*Tsuga heterophylla*, $\rho_{\text{ovenwood}} \approx 0.36 \text{ g cm}^{-3}$), and maple (*Acer saccharum*, $\rho_{\text{ovenwood}} \approx 0.72 \text{ g cm}^{-3}$) woods were obtained from a local supplier. $\rho_{\text{ovenwood}}$ is the density of oven-dry wood. Three groups of 5 samples for each species were prepared. The
samples were cut from the radial plane into wafers roughly 5 mm thick and 30 x 30 mm square, and the surfaces were sanded lightly to a smooth finish.

At first, the samples were dried in a convection oven for 48 hr at 103±2 °C to determine the oven-dry mass. Before and after the THz measurements, the samples were weighed (±0.01 g) in order to be certain that the samples did not absorb water from the atmosphere. The dimensions (length, width and thickness) of the samples were measured using digital calipers (±0.01 mm) before all THz measurements. After the measurement of oven-dry wood, the samples were conditioned at different relative humidities (RHs) to obtain different MCs. This was done in a step-wise approach using desiccators where the RH was controlled with saturated salt solutions. The salts used were: anhydrous calcium sulfate (CaSO₄, RH = 0%), potassium hydroxide (KOH, RH = 8%), potassium fluoride (KF, RH = 30%), sodium dichromate (Na₂Cr₂O₇·2H₂O, RH = 54%), ammonium chloride (NH₄Cl, RH = 77%) and potassium nitrate (KNO₃, RH = 94%) obtained from SIGMA-ALDRICH. A desiccator with water only was used for obtaining 99% RH. The samples were left for at least 48 hrs in the desiccators to ensure that they reached an equilibrium MC. After equilibrium was reached in the first step (RH = 11%), determined by no change in mass, the samples were removed and their mass and dimensions were recorded. THz measurements were taken immediately for two orientations of the THz field (parallel and perpendicular) with respect to the visible grain. The sample masses were recorded after THz measurements to ensure that the samples did not absorb or desorb water. After the THz measurements, the samples were placed in the next higher RH (that is, RH = 32%). Densities and MC were calculated from the physical dimensions and the averaged mass of the samples and mass of the oven-dry wood samples. This process was repeated for each MC progressing from
low to high MC. The experiments and wood conditioning were conducted at room temperature (21±1 °C).

3.3.2 THz spectral measurement

Polarized THz transmission spectroscopy was performed using a modified Picometrix T-Ray 4000 THz spectrometer. This system produces THz measurements in an 80 ps window at a rate of 1000 waveforms per second. The bandwidth extends from approximately 0.01-2.00 THz. For each species of wood studied, the time-domain waveforms of the transmitted terahertz radiation were recorded at 0° and 90° orientation of the grain with respect to the terahertz polarization, each measurement being an average of 10,000 waveforms. A reference THz signal without a wood sample in place was obtained prior to each transmission measurement. The sample sizes are chosen to be larger than the THz beam diameter to avoid diffraction effects. The THz spectroscopy was performed in transmission, with a THz beam diameter (1/e electric field) of approximately 30 mm. The complex refractive index of the samples was determined from a transmitted and reference THz pulse according to [39] in the thick sample approximation as outlined in [46]. The complex refractive index was used to calculate the dielectric function in order to apply the effective medium theories (EMTs) described in this work.

3.4 Results and discussion

Relation between dielectric function and oven-dry density and MC
Fig. 3.1 shows the moisture content change with relative humidity. Bound water exists in wood below the FSP, and behaves differently than free water as it is chemically bound by hydrogen bonding in the amorphous regions of the cellulose, hemicellulose and on the surface crystalline region of cellulose. Because the distribution of the chemical components does not vary greatly between species of wood, it is not expected that there are large differences in sorption behavior, which is reflected in Fig. 3.1.

![Fig. 3.1](image)

**Fig. 3.1** Dependence of moisture content (oven-dry basis) on the variation in relative humidity for maple (open circle), aspen (filled circle), birch (open square) and Western hemlock (filled square).

Fig. 3.2 shows the measured frequency-resolved (a) real part and (b) imaginary part of the dielectric function, $\varepsilon$, obtained from THz transmission spectroscopy of oven-dry wood. Plots (c) and (d) show the real and imaginary parts of the dielectric function averaged over the
frequency range of 0.1 to 0.2 THz, respectively. The THz beam is polarized perpendicular to the visible grain. A strong correlation between oven-dry density and $\varepsilon$ is observed consistent with other research [5, 14, 38, 55, 56]. The spectral range from 0.1 to 0.2 THz was used in this study in order to remain approximately in the wavelength range of validity for MG-EMT. As shown in Fig. 3.3, the real and imaginary part of $\varepsilon$ show a strong correlation with moisture content. These strong correlations between the real and imaginary part of $\varepsilon$ and oven-dry density and moisture content suggest the possibility of simultaneous prediction of both quantities from the measured THz signal.

Fig. 3.2 Frequency-resolved (a) real part and (b) imaginary part of the dielectric function obtained from THz transmission spectroscopy of oven-dry wood. Relation between oven-dry density and (c) real part and (d) imaginary part of dielectric function averaged over the frequency
range of 0.1 to 0.2 THz (polarization of the THz field is perpendicular to the grain of the wood samples).

![Graph showing frequency-resolved (a) real part and (b) imaginary part of the dielectric function obtained in transmission spectroscopy of Birch at various moisture content. Relation between moisture content and (c) real part and (d) imaginary part of dielectric function averaged over the frequency range of 0.1 to 0.2 THz (polarization of THz field is perpendicular to grain of wood).]

Fig. 3.3 Frequency-resolved (a) real part and (b) imaginary part of the dielectric function obtained in transmission spectroscopy of Birch at various moisture content. Relation between moisture content and (c) real part and (d) imaginary part of dielectric function averaged over the frequency range of 0.1 to 0.2 THz (polarization of THz field is perpendicular to grain of wood).

In order to extract a measurement of the density and moisture content from the THz measurement, a model is required that describes the dependence of the dielectric function on them. Next, a model is described that incorporates a Bruggeman EMT model combined with a
Maxwell-Garnet EMT (MG-EMT), and shown to be effective for extracting density and MC from THz measurements.

Simultaneous prediction of density and moisture content of wood species from THz measurements

A self consistent scheme (SCS) approximation of the elastic properties of materials [54], easily generalized to optical properties [57, 58], which specifically relates to a cylindrical geometry has been proposed by Hashin and termed the composite cylinder assemblage (CCA) scheme [54]. In this model, the effective medium properties are derived by inserting an infinite cylinder with dielectric function $\varepsilon_1$ in a concentric cylindrical shell of dielectric function $\varepsilon_2$, having radii $a$ and $\rho$, respectively, as shown in Fig. 3.4, and solving the boundary problem for the effective dielectric function ($\varepsilon_{\text{eff}}$) of the material.
Fig. 3.4 Composite Cylinder Assemblage (CCA) scheme where a cylindrical inclusion of dielectric constant is $\varepsilon_1$ surrounded by a cylindrical shell of dielectric constant $\varepsilon_2$ leading to a bulk effective dielectric function $\varepsilon_{\text{eff}}$.

In order for this calculation to be possible, the ratio of $\left(\frac{a}{\rho}\right)^3$ must be specified. Hashin has shown that by assuming this ratio is the volume fraction of particulate phase (of dielectric function $\varepsilon_1$), and therefore the concentric cylinders retain the volume fractions of the entire composite material, that a best possible upper bound on the effective dielectric function is given by (for the case where the field is polarized perpendicular to the axis of the cylinders):

$$\varepsilon_{\text{eff}}^{\perp,\text{max}} = \varepsilon_2 + \frac{f_1}{\frac{1}{\varepsilon_1 - \varepsilon_2} + \frac{f_2}{2\varepsilon_2}},$$

Eq. 3.1
Where \( \varepsilon_1 \) corresponds to properties of the core phase, and \( \varepsilon_2 \) corresponds to the properties of the matrix (shell) phase. This also happens to correspond to the MG formula used for analyzing cylindrical systems \([5, 58]\). The MG formula for infinite cylinders when the field is polarized perpendicular to the axis of cylindrical symmetry is usually written as:

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_2}{\varepsilon_{\text{eff}} + \varepsilon_2} = f_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2},
\]

Eq. 3.2

but is mathematically equivalent to Eq. 3.1. As is well known, the asymmetry in the MG expression (which is not symmetric under particle phase exchange: \( \varepsilon_2 \rightarrow \varepsilon_1 \)), leads to its applicability for low particulate phase volume fractions only. However, Hashin showed that under the CCA scheme, \( \varepsilon_2 \rightarrow \varepsilon_1 \) leads to the best possible lower bound for \( \varepsilon_{\text{eff}} \):

\[
\varepsilon_{\text{eff}}^{\text{min}} = \varepsilon_1 + \frac{f_2}{\frac{1}{\varepsilon_2 - \varepsilon_1} + \frac{1}{2\varepsilon_1}},
\]

Eq. 3.3

What is meant by best possible lower bound is that if it is only known that there is a cylindrical symmetry, and only volume fractions are known, then Equations 3.1 (or 3.2) and 3.3 are rigorous best possible bounds on \( \varepsilon_{\text{eff}} \)(which can only be improved upon with knowledge of geometrical distributions). For example, if it is known that the distribution of cylinders is periodic, a solution for \( \varepsilon_{\text{eff}} \) can be computed numerically, however, it will fall between these bounds \( (\varepsilon_{\text{eff}}^{\text{min}} < \varepsilon_{\text{eff}} < \varepsilon_{\text{eff}}^{\text{max}}) \) \([54]\).

The case where the field is polarized along the axis of the cylinders is more obvious, as the electric field is always parallel to the dielectric interfaces; it follows the simple mixing rule \([58]\):

\[
\varepsilon_{\text{eff}}^{||} = f_1 \varepsilon_1 + f_2 \varepsilon_2,
\]

Eq. 3.4
In this study, it is of interest to extend the model used previously for density of oven-dry wood [38] to include the effects of moisture, in particular, below the FSP. In this context, the geometry retains a cylindrical symmetry, and the MG-EMT (upper bound of the CCA) will be used to reflect this. However, the dielectric function of the cell wall material does change with moisture content as a result of the adsorption of bound water. Since the distribution of water in the cell wall is expected to be random (non-geometrical in nature), a Bruggeman EMT model to obtain an effective medium approximation for the hydrated cell wall seems appropriate. Indeed, an EMT was proposed to handle the incorporation of water within paper, which is a cellulose fiber network [52], and worked extremely well for predicting moisture content. The same approach is adopted here to handle the moisture within the cell wall material. The Bruggeman EMT is given by:

\[ \varepsilon_{\text{eff}} = \frac{1}{4} \left( \beta + \sqrt{\beta^2 + 8\varepsilon_1\varepsilon_2} \right), \]  
\[ \beta = (3\varepsilon_1 - 1)\varepsilon_1 + (3\varepsilon_2 - 1)\varepsilon_2, \]

Eq. 3.5

Eq. 3.6

In order for this to work, the dielectric properties of both the cell wall material, and the water in the cell wall must be known. It was found previously that a single (complex) value for the cell wall material could be assumed, allowing density prediction over 40 species of wood [38]. We adopt that value here (as discussed below). For the water, we use the well-known double Debye model appropriate for frequencies around 1 THz [59]:

\[ \varepsilon(\omega) = \frac{\varepsilon_s - \varepsilon_1}{1 - i\omega\tau_1} + \frac{\varepsilon_1 - \varepsilon_{\infty}}{1 - i\omega\tau_2} + \varepsilon_{\infty}, \]

Eq. 3.7

Where the parameters for Eq. 3.7 were taken as presented in Ref. [59]: \( \varepsilon_s = 73.36, \varepsilon_1 = 5.16, \tau_1 = 7.89 \) ps, \( \varepsilon_\infty = 3.49, \) and \( \tau_2 = 0.181 \) ps.
The overall model can be described as follows (refer to Fig. 3.5). The dielectric function of the wet cell wall material is calculated using the Bruggeman model (Eq. 3.5 and 3.6) to combine the cell wall material and water, which combine in a non-geometric fashion. The wet cell wall material then makes up the host for a cylindrical symmetry similar to what is seen in Fig. 3.4. Therefore a MG-EMT with cylindrical symmetry is applied (Eq. 3.2), and the effective dielectric constant of the wood is obtained by combining the dielectric constant of air and wet cell wall material using the MG-EMT.
Fig. 3.5 Effective medium theory applied to determine the bulk effective dielectric function of wood at different moisture contents. The dry cell wall material with dielectric constant $\varepsilon_{\text{ovencw}}$ (which is known from measurement – see text for details) is combined with a random distribution of water assumed to have a dielectric function $\varepsilon_{\text{water}}$ (see text for details) using the Bruggeman model to determine the effective dielectric constant of the wet cell wall material. The MG model with cylindrical symmetry is then applied to combine air, with a dielectric function $\varepsilon_{\text{air}}$, and the wet cell wall material to determine the effective dielectric constant of the wood, $\varepsilon_{\text{wetwood}}$.

In the first step of computing the dielectric function of the cell wall material, the geometry is unimportant, and so nothing changes with the polarization of the THz field. In contrast to this, the step of computing the effective dielectric function of the wood from the wet cell wall material and air is polarization-dependent. When the THz field is polarized
perpendicular to the grain, the MG step requires use of Eq. 3.1, whereas when the field is polarized parallel to the axis of cylindrical symmetry, Eq. 3.4 is used.

This model can be used to simultaneously measure the density and moisture content (by obtaining the volume fractions $f_a$ and $f_w$) of wood samples as follows. A matrix of volume fractions $f_a \times f_w$ is formed over the region of interest ($f_a$: from 0.3 to 0.8 with 0.005 steps, $f_w$: from 0 to 0.3 with 0.005 steps). The dielectric function of the wood is evaluated using the EMT described above, giving $\epsilon_{\text{eff}}$ for each combination of $f_a$ and $f_w$. The availability of a reference scan then allows the prediction of the transmitted THz waveform as follows. Defining the Fresnel transmission coefficients from incident material $i$, to transmitted material $t$:

$$t_{it} = \frac{2n_s}{n_i + n_t}, \quad \text{Eq. 3.8}$$

where $n$ is the index of refraction, and $t_{it}$ is the Fresnel transmission coefficient at normal incidence. The complex, frequency-dependent transmission function ($T(f)$) can then be represented in terms of the complex index of refraction of the wood ($\tilde{n}_{\text{wood}} = \sqrt{\epsilon_{\text{eff}}}$), calculated from $\epsilon_{\text{eff}}$, and given by:

$$T_{\text{wood}}(f) = t_{\text{aw}} t_{\text{wa}} e^{i2\pi fd(\tilde{n}_{\text{wood}}^{-1})}, \quad \text{Eq. 3.9}$$

where $f$ is the frequency, and $d$ is the thickness of the wood sample. The effect of the wood sample on the reference in the frequency domain is given by:

$$E_{\text{wood}}(f) = T_{\text{wood}}(f) E_{\text{ref}}(f), \quad \text{Eq. 3.10}$$

And thus, the predicted THz waveform in the time-domain is calculated by inverse Fourier transformation:
We then define a measure of error in the predicted waveform in terms of the sum of squared difference from the measured waveform:

\[ \text{Err} = \sum_l \left( E_{\text{wood}}^{\text{pred}}(t) - E_{\text{wood}}^{\text{meas}}(t) \right)^2 , \]

Eq. 3.12

The only free parameters in the model are the volume fractions of air and water, and the value of the dielectric function of the cell wall material and water. As discussed above, the dielectric function of water is taken from ref [60] and is held fixed.

The dielectric function of the dry cell wall material is obtained from the measured values of permittivity of oven-dry aspen, birch, hemlock and maple. The indices of refraction and absorption coefficients were determined and averaged over the frequency range of 0.1 to 0.2 THz. The complex dielectric function \((\epsilon = \tilde{n}^2)\) was calculated from the THz measurements\((\tilde{n} = n + ik)\). By applying equations (3.2) or (3.4) for the different polarization orientations, the dielectric function of the oven-dry cell wall material was inferred. The calculated dielectric functions of the cell wall material of the 4 species of wood were averaged over the frequency range of 0.1 - 0.2 THz. For the case when the THz field is polarized parallel to the visible grain, the average of \(\epsilon_{\text{oven}cw}\) over 4 species was 3.36+0.18i, while \(\epsilon_{\text{oven}cw}\) was 3.39+0.19i when the THz field is polarized perpendicular to the visible grain. We took the dielectric function of the dry cell wall as these frequency-independent values.

Reference and transmitted THz waveforms transmitted through samples of aspen wood, whose density is 0.50 g cm\(^{-3}\) and MC = 2.07%, measured with the THz field polarized perpendicular to the visible grain is shown in Fig. 6. Predicted THz waveform gave minimum
error in terms of the sum of squared difference from the measured waveform when the value of \(f_a = 0.635\) and \(f_w = 0.01\) were used. The predicted THz waveform is also shown in Fig. 3.6. The volume fractions \(f_a\) and \(f_w\) obtained were converted to density using the formula,

\[
\rho_{\text{wetwood}} = \rho_{\text{air}} \times f_a + \rho_{\text{ovenCW}} \times f_{\text{ovenCW}} + \rho_w \times f_w, \quad \text{Eq. 3.13}
\]

where, \(f_{\text{ovenCW}}\) is the volume fraction of the oven-dry cell wall material \((f_{\text{ovenCW}} = 1 - (f_a + f_w))\), \(\rho_{\text{wetwood}}\) is the density of wet wood, \(\rho_{\text{ovenCW}}\) is the average density of the oven-dry cell wall material, which is assumed to be 1.4 g cm\(^{-3}\) [42], \(\rho_w\) is the density of water which is taken to be 1 g cm\(^{-3}\), and \(\rho_{\text{air}}\) is the density of air which is taken to be 0.0012 g cm\(^{-3}\) at 20 °C.

Moisture contents were calculated using the formula,

\[
\rho_{\text{ovenwood}} = \rho_{\text{air}} \times (f_a + f_w) + \rho_{\text{ovenCW}} \times f_{\text{ovenCW}}, \quad \text{Eq. 3.14}
\]

\[
MC = \left(\frac{\rho_{\text{wetwood}} - \rho_{\text{ovenwood}}}{\rho_{\text{ovenwood}}}\right) \times 100 \ (%), \quad \text{Eq. 3.15}
\]

where, \(\rho_{\text{ovenwood}}\) is density of oven-dry wood, MC is moisture content of wood. The predicted values that minimized the error function (Eq. 3.12) for the waveform of Fig. 3.6 gave \(f_a\) and \(f_w\) corresponding to a MC = 2.01% and \(\rho_{\text{wetwood}} = 0.51\) g cm\(^{-3}\).
Fig. 3.6 Typical set of reference (dot line) and sample (solid line) waveforms along with the best-fit predicted wave (dashed line) according to the model.

Fig. 3.7 shows the relationship between the measured and predicted density using EMT and the measured THz signal. The model provides very good prediction, with a determination coefficient value $r^2 = 0.98$ and 0.96 and root mean square error (RMSE) values are 0.020 and 0.030 (corresponding to 0.028 g cm$^{-3}$ and 0.030 g cm$^{-3}$) for perpendicular and parallel polarization geometries, respectively. Determination coefficient value and RMSE were calculated using:

$$r^2 = 1 - \frac{\sum (y-y_{\text{pred}})^2}{\sum (y-\bar{y})^2}, \quad \text{Eq. 3.16}$$

$$\text{RMSE} = \sqrt{\frac{\sum (y-y_{\text{pred}})^2}{n-2}}, \quad \text{Eq. 3.17}$$

where, $y$ is measured value, $y_{\text{pred}}$ is predicted value from THz, $\bar{y}$ is average value of measured
value and \( n \) is the number of samples.

Fig. 3.8 shows the relationship between the measured and predicted MC. For both polarization configurations, the MC was consistently underestimated at low MC, and approached correct value at high MC. This can be understood based on the behavior of the dielectric function for water as the amount of bound water increases to approach the FSP. In particular, free water absorbs much more strongly than bound water, and so at low moisture contents, the use of the highly attenuating free water dielectric function will result in systematic under estimation of the MC. In contrast, as the amount of free water increases, the estimation will tend to get better and closer to the real value as the fraction of total water that is free increases. Furthermore, as shown in Fig. 3.3, the real part of dielectric function linearly increases with MC, whereas the imaginary part shows a quadratic increase. This implies that the imaginary part of the dielectric function for bound water is indeed a function of MC. The stronger absorption at THz frequencies of free water in comparison to bound water has been described in detail for hydrated lipid systems [61], and was also directly observed in wood composite systems [53] for MCs below the FSP. In order to incorporate the MC dependence of the dielectric function of water into our model, it would be necessary to know the dependence in detail. Since this information is not known at present, it is beyond the scope of the work presented here.

The main results presented here (Fig. 7 and 8) demonstrate that THz-TDS can be used for non destructive and accurate measurements of wet wood density over a range of MCs for the wood species studied here. In addition, the correlation between predicted and measured MCs indicates that simultaneous MC measurement is possible. In order to accurately predict MC without a calibration procedure of some type, however, a more detailed model of the dielectric function of water as a function of MC is required. It should be noted that this behavior could be
expected to be species-dependent, at least in part because of the different surface areas exposed
to air in each species (i.e. different porosities). Using both the real part and the imaginary part of
the measured complex dielectric function therefore provides the possibility of simultaneous
measurement of density and MC when the sampling area covers several annual growth rings.

Fig. 3.7 Relationship between measured and predicted density based on MG-EMT model. $r^2$,
determination coefficient; RMSE, root mean square error. (a) Perpendicular and (b) parallel refer
to the polarization of the THz field with respect to the grain of the wood samples.
Fig. 3.8 Relationship between measured and predicted moisture content based on MG-EMT model. $r^2$, determination coefficient; RMSE, root mean square error. Perpendicular and parallel refer to the polarization of the THz field with respect to the grain of the wood samples.

Several different EMT models have been used to study properties of composite materials at terahertz frequencies [62]. It is somewhat commonplace in the THz literature to choose an EMT that best fits the experimental data [63]. Therefore, it is appropriate to review different EMT models in relation to what has been used here.

A comprehensive review of different EMT models that have been used for THz applications has been published previously [62]. The geometry-independent models suitable for use as the mixing rule for the wet cell wall material (water + cell wall material) are the Bruggeman model, and the Landau, Lifshitz, Looyenga (LLL) model [62]. While the latter can be used for mixtures with large dielectric contrast [53], the former model has been applied here as it worked exceptionally well for water in paper [52], which is chemically similar to the wood
cell wall material. The second component of the model is the geometry-dependent component suitable for a cylindrical symmetry exhibited by wood structure. When the THz field is polarized parallel to the visible grain, then the THz field will always lie in the boundary between two interfaces, and so follow the simple mixing rule given by Eq. 3.4 [58]. That this model gives good agreement for the density prediction across moisture contents of Fig. 7 is evidence that the Bruggeman model is appropriate for the cell wall material.

For the polarization of the THz field perpendicular to the axis of cylindrical symmetry, in addition to the MG-EMT used previously [38], there is the Polder and van Santen (PvS) model for rod-like shapes, and a modified Bruggeman model appropriate for rods [62] that could be appropriate for wood related to the work presented here. The PvS and modified Bruggeman models lead to dielectric functions that lie within the bounds of Eqs. 3.1 and 3.3, and in practice, we find that the predictive power of the model gets progressively worse with models that move away from the upper bound and towards the lower bounds described by Eqs. 3.1 and 3.3.

3.5 Conclusion

Moisture content and density of 4 species of wood were simultaneously measured by means of THz time domain spectroscopy. The real and imaginary parts of the complex dielectric function have a strong correlation with density and moisture content. A model combining Bruggeman and MG EMTs was proposed and shown to have good predictive power for density and MC simultaneously. It was observed that the results for predicting the MC imply that the dielectric function of water in wood changes as a function of moisture content as the water goes from bound at low MC to free at high MC, consistent with other reports. In order to predict MC
beyond correlations, it was determined that more work is required to understand the MC dependence of the dielectric function of water in wet wood. The ability to simultaneously measure density and MC over a range of MCs below the fiber saturation point make THz radiation an attractive new technology for probing wood properties.
Chapter 4

Investigation of the moisture content desorption in wood by terahertz time-domain spectroscopy

4.1 Abstract

Terahertz time-domain spectroscopy was used to investigate the dielectric constant of water in 4 wood species (Aspen, Birch, Hemlock and Fir) at different moisture contents. Applying THz-TDS, changes in the absorption coefficient and refractive index of water absorbed into wood are observed and characterized. An effective medium theory was applied to determine the effective dielectric function of wood at frequencies between 0.1 and 0.5 THz at different moisture contents. A model was proposed to describe the dependence of the dielectric function of water on the varying moisture content.
4.2 Introduction

Wood is a hygroscopic material whose moisture content (MC) depends on the surrounding relative humidity (RH) and temperature (T). Wood swells (or shrinks) in response to increasing (or decreasing) MC. When wood is exposed to a fixed relative humidity at constant temperature, the wood will develop the same MC as the surrounding atmosphere, which is known as the equilibrium moisture content (EMC). Moisture content in this study is defined as the dry-basis MC, which is the percentage difference between the wet mass and the oven-dried mass [38, 64].

\[
MC = \left(\frac{m-m_{od}}{m_{od}}\right) \times 100\%, \quad \text{Eq. 4.1}
\]

where \(m\) is the wet mass and \(m_{od}\) is the oven-dry mass.

Wood is made from polymers, that is, hemicellulose, cellulose, and lignin, which are all more or less hydrophilic. The hydroxyl groups are the most important component responsible for the wood-water interactions. Carboxyl groups are another chemical component than can attract water. All chemical groups that are able to attract water molecules are called sorption sites.

In a living tree, water in wood can be held as non-freezing bound water, freezing bound water, and free water. Non-freezing bound water is the water bound to the sorption sites. Freezing bound water is more loosely bound than non-freezing bound water. The freezing bound water can be found at MCs down to at least 8% MC. Free water is that which exists in the cell lumen voids or free space which is held in the amorphous region within the cellulose, hemicellulose and on the surface crystalline region of cellulose by hydrogen bonding [58]. When wood is dried, the free water evaporates into the atmosphere until the fiber saturation point (FSP) is reached, which occurs at a MC usually in the range of 25 to 30% where only bound water is present in the wood structure. Also, the FSP is known as the point where the maximum amount
of water is held within the wood cell wall. Bound water behaves differently than the free water, as it can be chemically bound to the cell wall by intermolecular hydrogen bonds with the hydroxyl groups. Therefore, many physical properties of wood change significantly below the fiber saturation point, and the variation in MC during the manufacturing process is extremely important to understand [59].

Previous experiments that measure EMC in wood at THz frequencies do not take into consideration the dielectric function of bound water but use only the dielectric function of free water when implementing an EMT resulting in underestimation of the measured MC as shown in our previous work [65]. For this reason, studying the dependence of the dielectric function of water on MC is important. Recently, many experiments were conducted for studying the behaviour of the dielectric function of bound water in different materials. A model for the dielectric function of bound water in soil was successfully introduced for applications in microwave remote sensing [66]. The dependence of the complex permittivity of water on frequency and kernel moisture content was studied at radio and microwave frequencies [56]. The physical and mechanical properties of a polymer are strongly affected by the amount of water [67]. For this reason, the water content in a polymer is an important parameter to be studied [67]. An effective medium theory was applied to calculate the effective dielectric constant of the material. The dielectric constant of wood is also strongly affected by MC and a good prediction for the MC in wood is extremely important to the wood industry. To achieve a good prediction for MC in wood, the dielectric function of bound water in wood at different MCs should be studied.

Terahertz time-domain spectroscopy (THz-TDS) is one of the commonly used techniques that is showing promise as a powerful tool in wood science [5]. This is because wood
is relatively transparent at these frequencies (below about 1 THz). The advantage of using THz-TDS relies on its ability to study the structures involved (the wavelength at 1 THz is 300 μm, and so millimeter spatial resolution is possible), the sensitivity of THz radiation to the grain structure of wood (wood is extremely birefringent in the far-infrared), and the strong sensitivity of THz radiation to water allows probing of dynamics of water in wood. The dielectric relaxation response of water in the THz frequency range contains information on how well the permanent dipoles associated with water molecules can keep up with oscillating fields of a certain frequency [65]. When an electric field is applied, the permanent dipoles \( \vec{p} \) associated with the water molecules will tend to align with the applied field, resulting in an induced polarization [65].

\[
\vec{\rho} = \sum \vec{p} = (\varepsilon - \varepsilon_0)\vec{E}, \tag{4.2}
\]

where \( \varepsilon_0 \) is the vacuum permittivity. The water molecules tend to reorient themselves to align their dipole moments with the oscillating electric field. If the field frequency is larger than the reorientation frequency of the water molecules, alignment becomes difficult and the induced polarization, and subsequently, the dielectric constant decreases. Hence, the frequency dependent dielectric response contains information about the reorientation dynamics of water molecules [65]. Water molecules can have slower dynamics due to interaction with other materials. In this case, the water molecules become irrotational, which is referred as "bound water".

In a previous study, the prediction of oven-dry density of 46 wood species was successful using THz time-domain spectroscopy over a large range of volume fractions (\( f = 0.2-0.8 \)) by applying a Maxwell Garnett (MG) effective medium theory (EMT) [38]. The work was extended to include a simultaneous prediction of density and MC over a range of MC's below the fiber saturation point [65]. For both polarization configurations, the MC was consistently underestimated at low MC, and approached the correct value at high MC as shown in Fig. 1 of
Reference [65]. It is known that liquid water absorbs more strongly than bound water, and using a free water dielectric function at low MC results in systematic under estimation of the MC. As the MC increases, the amount of free water increases and the estimation will tend to get closer to the actual value. Recently, a comparison between the absorption of free water and bound water at THz frequencies has been described in detail for hydrated lipid systems [56]. At the present time, the physical characteristic of bound water in wood at THz frequencies has not been studied in detail. Bound water has been considered to have an ice-like structure (which is irrotational) because of the hydrogen bonding. In order to improve the accuracy of MC prediction using THz-TDS, a model of the MC-dependent dielectric function of water is required. This problem is the focus of the present work.

Experiments have identified that, the relaxation time of bound water molecules $\tau_{bw}$ is different from the relaxation time of free water $\tau_w$ and ice molecules $\tau_{i}$ [66]. This is because bound water molecules form hydrogen bonds with the sorption sites in the wood cell wall and play a significant role in increasing the relaxation time of the water molecules. Accordingly, the dielectric constant for bound water is lower than that for free water. The dielectric constant of bound water also changes depending on how many monomolecular layers of water exist in a system [66]. In this work, an experiment is conducted to show the relationship between the dielectric constant of water and MC in wood.

4.3 Materials and Methods

4.3.1 Sample preparation

As described in Chapter 3, a similar sample preparation was undertaken. Aspen ($Populustremuloides$, $\rho_{ovenwood} \sim 0.49\ g.cm^{-3}$), birch ($Betula$ spp, $\rho_{ovenwood} \sim 0.64\ g.cm^{-3}$),
Western hemlock (*Tsuga heterophylla*, $\rho_{\text{ovenwood}} \approx 0.36 \text{ g.cm}^{-3}$), and fir (*Abies*, $\rho_{\text{ovenwood}} \approx 0.30 \text{ g.cm}^{-3}$) woods were obtained from a local supplier. $\rho_{\text{ovenwood}}$ is the density of oven-dry wood. Four samples for each species were prepared. The samples were cut from the radial plane into wafers roughly 1 mm thick and 30 x 30 mm square, and the surfaces were sanded lightly to a smooth finish.

Initially, the samples were dried in a convection oven for 24 hr at 103±2 °C for THz measurements from oven dry (MC ≈ 0%) up to air dry (MC ≈ 5%). The samples were weighed (±0.001 g) before and after each THz measurement to ensure that MC did not change during the measurements. The dimensions (length, width and thickness) of the samples were measured using digital calipers (±0.01 mm) before all THz measurements. THz measurements were repeated 10 times for every MC and averaged. A difference in MC of 1% between subsequent measurements was obtained by allowing the samples to be exposed to atmosphere for a period of time. After these measurements at low MC, the samples were fully saturated by immersion in water under full vacuum for at least 24 hrs. After reaching saturation, the samples were removed and their mass and dimensions were recorded. THz measurements were taken immediately from MC at saturation to air dried MC so that the entire range of MC up to the FSP was studied. All measurements were taken with the THz field polarized parallel to the visible grain. Densities and MC were calculated from the physical dimensions and the mass of the samples and mass of the oven-dry wood samples (see Eq. 1). The experiments and wood conditioning were conducted at room temperature (21±1°C).

4.3.2 THz spectral measurement

THz transmission spectroscopy was performed using a modified Picometrix T-Ray 4000 THz spectrometer. This system collects waveforms over an 80 ps window at 1000 Hz with a
bandwidth that extends from approximately 0.01-2.00 THz. The measurements were recorded at 0° orientation of the grain with respect to the THz field polarization, each measurement being an average of 5,000 waveforms. Before each transmission measurement a reference THz signal without a wood sample in place was obtained, and a background waveform recorded. The THz spectroscopy was performed using a transmission geometry, with a THz beam diameter (1/e electric field) of approximately 30 mm. The complex refractive index of the samples was determined using [39] as discussed in section 2.10.3. The complex dielectric function of wood was obtained from the measured complex refractive index in order to apply the effective medium theories (EMTs).

4.4 Results and discussion

In the THz time-domain spectroscopy experiments, the presence of water in wood leads to a reduction of the THz pulse amplitude and a temporal shift of the THz pulse. These two values can be related to the frequency-dependent complex refractive index of wood. Fig. 4.1 shows a typical terahertz wave as it passed through wood at varying MC from 0% to 30%. As shown in this figure, the THz field decreases with increasing MC.
Fig. 4.1 Dependence of the THz field amplitude on the variation of MC in wood. These data are taken at MCs between 0% and 30%.

The time-domain data was Fourier transformed to the frequency domain and the complex refractive index at each MC was obtained at: $\varepsilon(\nu) = \hat{n}^2(\nu)$. Fig. 4.2 shows the measured frequency-resolved real part of the dielectric function, $\varepsilon$, obtained from THz transmission spectroscopy of four different wood species at different MCs when the grain is parallel to the THz field. Fig. 4.3 shows the measured frequency-resolved imaginary part of the dielectric function, $\varepsilon$, when the grain is parallel respect to the THz field. Both the real and imaginary parts of the effective dielectric function of wood are changing monotonically with MC. At low MC (below 10% MC), the water is mostly bound, and at high MC (above about 30% MC), the water is mostly free, so one expects that the dielectric function of water in wood to change with MC.
Fig. 4.2 Real part of the dielectric function between 0.2 and 0.5 THz obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir, for the parallel orientation of the wood grain with respect to THz field polarization at MC between 0% and 30%.
Fig. 4.3 Imaginary part of the dielectric function between 0.2 and 0.5 THz obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir, for the parallel orientation of the wood grain with respect to THz field polarization at MC between 0% and 30%.

In Fig. 4.4, the real part of the dielectric function of wood is shown as a function of MC, and Fig. 4.5f shows the imaginary part as a function of MC, both at a frequency of 0.3 THz. As shown in the figures, the real and imaginary parts are dependent on the MC in the wood species studied.
Fig. 4.4 Real part of the dielectric function of wood obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz.
Fig. 4.5 Imaginary part of the dielectric function of wood obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz.

In order to extract a measurement of the dielectric constant of water from the THz measurements, a model was required that described the dependence of the dielectric constant. A simple Bruggeman effective medium theory (EMT) model was used here, and shown to be effective for extracting dielectric constant of water from THz measurements at different MCs, using two different measurements whose MC do not differ substantially.
Prediction of dielectric function of bound water from THz measurements

The effective dielectric function of wood changes approximately linearly with moisture content as a result of the increasing amount of bound water as in Fig. 4.2 and 4.3. Consider a simplistic view that the wood cell wall has a cylindrical geometry and the distribution of water in the cell wall is expected to be random (non-geometrical in nature). In this case, a Bruggeman EMT model is appropriate to obtain an effective medium approximation for the hydrated cell wall if two samples are compared with similar MCs; this can be described by [25]:

\[ \varepsilon_{\text{eff}} = \frac{1}{4} \left( \beta + \sqrt{\beta^2 + 8\varepsilon_1\varepsilon_2} \right), \]  
\[ \beta = (3f_1 - 1)\varepsilon_1 + (3f_2 - 1)\varepsilon_2, \]

where \( \varepsilon_1 \) is the dielectric constant of the first material, \( \varepsilon_2 \) is the dielectric constant of the second material, \( \varepsilon_{\text{eff}} \) is the effective dielectric constant of the mixture, \( f_1 \) is the volume fraction of the first material, and \( f_2 \) is the volume fraction of the second material. In order to obtain the dielectric constant of water at a certain MC, we need to measure the dielectric constant of wood at two slightly different MCs.

The Bruggeman model is used (Eqs. 4.3 and 4.4) with \( \varepsilon_1 \) taken to be the dielectric constant of the lower MC sample, \( \varepsilon_{\text{eff}} \) taken to be the dielectric constant of the (slightly) higher MC sample, and \( \varepsilon_2 \) is taken to be the dielectric constant of water. Knowing the mass of water in the two samples allowed for the calculation of the appropriate volume fractions, and measurements for \( \varepsilon_1 \) and \( \varepsilon_{\text{eff}} \) from the THz spectra allow the calculation of the dielectric function of water (\( \varepsilon_2 \)).

For comparison, the dielectric constant if ice [68] and liquid water [69] are presented as the upper and lower solid curves in the figures that follow respectively.
Fig. 4.6 The real part of the dielectric constant of water at MCs from 1% up to 29% for the four wood species: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The upper thick line represents the real part of the dielectric constant of free water and the lower thick line represents the real part of the dielectric constant of ice as per references [68, 69] respectively.
Fig. 4.7 The imaginary part of the dielectric constant of water at MCs from 1% up to 29% for the four wood species: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The upper thick line represents the imaginary part of the dielectric constant of free water and the lower thick line represents the imaginary part of the dielectric constant of ice as per references [69, 68] respectively.

As shown in Figs. 4.6 and 4.7, the dielectric constant of water varies with MC. The water molecules which are added to the wood at the lowest MC are tightly bound to the wood surface. As such they will have a larger relaxation time and consequently a lower dielectric constant. As more water is added, the molecules are further away from the wood surfaces and are more free to rotate. Consequently, they will have a shorter relaxation time, which results in a larger dielectric constant. According to a simple Debye model (Eq. 4.5) [66], the relaxation time depends linearly on the thickness of the water film, which in turn depends on the effective surface area onto which the water is adsorbed. Since the surface area in wood varies for the different wood species, it is expected that the relationship between the dielectric constant of
water and moisture content is also dependent on the wood species. Hardwoods have a larger surface area and will be able to hold more water molecules in close proximity to the cellulose, hemicellulose and lignin, than softwoods. The larger surface area results in a higher FSP for hardwoods (Aspen, Birch) than softwoods (Fir, Hemlock).

A relationship for the relaxation time of bound water using Debye model for the dielectric function of water in soil and thickness of the water film covering the soil particles has been reported and reproduced here in Eq. 4.5 [66]:

$$\tau_{bw}(+27^\circ C) = \left(-4.9648 \times 10^{24} h^2 - 3.0867 \times 10^{11} \ln(h) - \frac{7.592 \times 10^3}{h} + 3.9121 \times 10^{18} h - 5.2036 \times 10^{12}\right)^{-1}, \quad \text{Eq. 4.5}$$

where $\tau_{bw}$ is the relaxation time for bound water (s), and h is the water film thickness (cm).

This dielectric function changes from that expected for bound water (similar to ice) at very low MC, and increases to what is expected for free water before the MC reaches the fiber saturation point (approximately 30% MC for the case of soil). The change in the amount of bound water in wood leads to a change in its dielectric properties due to a change in the relaxation time of water molecules (see Eq. 4.5). Below 5% MC, water molecules that enter the system will result in less swelling while above 5% MC the degree of swelling increases which indicates that a greater number of hydrogen bonds are broken (sorption sites) per entering water molecule [70]. New hydrogen bonding is formed with the water molecules which result in increasing the relaxation time, and according to a Debye model [59], the dielectric function of water decreases (Fig. 4.6 and Fig. 4.7). At a certain moisture content, the dielectric properties of bound water in wood become similar to the dielectric properties of free water and no further increase in moisture content is expected to change the dielectric properties. This occurs when all sorption sites within the cell wall are bound to water molecules. In this case, water molecules
start to fill the cell wall voids, which are considered free water, and the dielectric function of water at this MC is equal to that of free water. It is clear from the observed behavior that water in wood is not just going onto the surface of the wood within the porous structure, but also penetrates the cell wall. If this were not the case, the dielectric function of water would be reached at extremely low MC. This implies an extremely large surface area for sorption, and is consistent with the variation in physical properties (shrinkage and swelling) that occurs for MC’s below the FSP. The variation of surface area within wood species may explain the relationship between the dielectric function of water and MC for the studied wood species. In particular, Figures 4.6 and 4.7 show that the dielectric constant of water approaches that of liquid water more rapidly (in terms of MC) for Hemlock and Fir (softwoods) in comparison to Aspen and Birch (hardwoods), which is consistent with the larger FSP, and therefore larger surface areas, of hardwoods. Therefore the behavior of water in wood at different MCs is giving information about the microstructure of the wood itself.

In Figs. 4.8 and 4.9, the real and imaginary parts of the dielectric function of water were plotted as a function of MC at frequency 0.3 THz. As shown in the figures, the real and imaginary parts are dependent on the MC in the wood species under study.
Fig. 4.8 Real part of the dielectric function of water obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz. The red and blue asterisks represent the dielectric constant of ice and free water respectively.
Fig. 4.9 Imaginary part of the dielectric function of water obtained from THz transmission spectroscopy of 4 different wood species which are: (a) Birch, (b) Aspen, (c) Hemlock, and (d) Fir. The polarization of the THz field is parallel to the wood grain, and the results are plotted for a frequency of 0.3 THz. The red and blue asterisks represent the dielectric constant of ice and free water respectively.

4.5 Conclusion

The dielectric constant of water at different moisture contents in 4 species of wood was measured. The real and imaginary parts change with moisture content. A Bruggeman model was used to study the dependence of the dielectric constant of water on moisture content. The dielectric function of water is consistent with bound water at low MC (similar to ice) and
approaches that of free water at higher MCs. Sorption sites attract water molecules by forming hydrogen bonds, resulting in the presence of bound water. At a certain MC, when all sorption sites are full, water molecules start to fill the cell wall voids as free water. The dielectric function of water in wood varies between species depending on the number of sorption sites that exist in the wood. The number of sorption sites depends on the effective surface area within the wood, which is different between species. The dielectric function of water in wood at different MC's is therefore a probe of the microstructure of the wood. Further improvement in prediction of moisture content in wood using THz-TDS is expected by considering the variation of the dielectric function of water with moisture content within the different wood species.
Chapter 5

Conclusion

Moisture content and density of 4 wood species were simultaneously measured by means of THz time domain spectroscopy. A strong correlation of the real and imaginary parts of the complex dielectric function can be observed with density and moisture content. A new model combining Bruggeman and MG EMTs was introduced and shown to have good predictive power for predicting density and MC using THz-TDS. The results for predicting the MC, however, showed a consistent underestimation at low MC's which imply that the dielectric function of water in wood is different than the assumed values for free water, indicating that bound water plays a significant role in THz-wood interactions.

More work was necessary to understand the MC dependence of the dielectric function of water in wet wood. For this reason, the dielectric function of water in wet wood was investigated in different wood species. The real and imaginary parts were shown to change with moisture content. A Bruggeman EMT was used to extract the dielectric function of water in wet wood as a function of MC. The dielectric function was seen to grow monotonically (both the real and imaginary parts) with MC. This change was seen to exhibit a dielectric function close to that
of ice for purely bound water at low MC, and move towards the dielectric function of liquid (or free) water at MCs near the FSP.

From the results presented here, it was found that the density and moisture content of wood could be probed by THz-TDS. Further improvement in predicting the moisture content in wood can be achieved by developing a theoretical model for the relaxation time of water within wood that takes into account the microstructure of that wood. The studies made on the dependence of the dielectric function of water in wood with moisture content can be extended to include a wide range of different wood species with different microstructures. This would help to clarify the effect of wood surface area on the dielectric function of water. Another area of future work would be to determine a precise method for measuring the FSP in different wood species using THz-TDS based on the behaviour of water in wood at different MCs.

A final area of future work would be applying the variation of the dielectric function of water with moisture content within wood species in future experiments may allow more accurate simultaneous measurements of density and moisture content in wood.
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