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Dielectric Characterization of Bentonite Clay at Various Moisture Contents and with Mixtures of Biomass in the Microwave Spectrum

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Abstract:	This study assesses the potential for using bentonite as a microwave absorber for microwave-assisted biomass pyrolysis based on the dielectric properties. Dielectric properties of bentonite at different moisture contents were measured using a coaxial line dielectric probe and vector network analyzer in the microwave frequency range from 0.2 to 4.5 GHz at room temperature. Additionally, dielectric properties of mixtures of bentonite with biomass were measured from 1.5 to 20 GHz. As expected, both dielectric constant and dielectric loss factor increased linearly with increasing moisture content. Measurements on biomass and bentonite mixtures show a quadratic increase in dielectric constant and loss factor with increasing bentonite content and with moisture contents ranging from 9.5% (pure bentonite) to 11.4% (pure biomass) wet basis. At 915 MHz, dielectric constant ranged from 2.0 to 6.2 and dielectric loss ranged from 0.2 to 2.7 respectively. At 2450 MHz, dielectric constant ranged from, 1.8 to 5.1, and dielectric loss ranged from 0.7 to 2.6, respectively.



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SUBMISSION OF MANUSCRIPT FOR PUBLICATION CONSIDERATION IN *JOURNAL OF MICROWAVE POWER AND ELECTROMAGNETIC ENERGY (JMPEE)*

Please find enclosed a manuscript entitled, "Dielectric Characterization of Bentonite Clay at Various Moisture Contents and with Mixtures of Biomass in the Microwave Spectrum" for consideration for publishing as an article in *JMPEE*. The contributing authors to this manuscript are as follows: Candice Ellison, Murat McKeown, Samir Trabelsi, Cosmin Marculescu, and Dorin Boldor. I attest that the work done is original and it has not in whole or in part been submitted for publication in any other journal.

The research presented in the attached manuscript details fundamental and novel work on characterizing dielectric properties for biomass and bentonite mixtures at microwave frequencies between 0.5 to 20 GHz. It expands on the existing body of knowledge of characterizing dielectric properties of materials, while contributing unique insights into mixtures of bentonite and biomasses. The work presented recognizes that biomasses tend to be low loss material, resulting in poor dielectric heating. This makes high temperature thermochemical conversion processes using microwaves very energy intensive. Bentonite, however, has greater dielectric loss, resulting in greater susceptibility to microwave heating. Mixtures of bentonite with biomass can improve the energy efficiency of thermochemical conversion via microwave heating. Dielectric measurements of these mixtures allow for greater understanding and optimization of microwave-assisted conversion of biomass to biofuels and provide insight into secondary use of bentonite.

We thank you very much for the opportunity to submit our research work to your esteemed journal. Please feel free to contact me if you have any questions related to this work.

Sincerely,

A handwritten signature in blue ink, appearing to read "Dorin Boldor", is placed over a light blue rectangular background.

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DIELECTRIC CHARACTERIZATION OF BENTONITE CLAY AT VARIOUS MOISTURE CONTENTS AND WITH MIXTURES OF BIOMASS IN THE MICROWAVE SPECTRUM

ABSTRACT

This study assesses the potential for using bentonite as a microwave absorber for microwave-assisted biomass pyrolysis based on the dielectric properties. Dielectric properties of bentonite at different moisture contents were measured using a coaxial line dielectric probe and vector network analyzer in the microwave frequency range from 0.2 to 4.5 GHz at room temperature. Additionally, dielectric properties of mixtures of bentonite with biomass were measured from 1.5 to 20 GHz. As expected, both dielectric constant and dielectric loss factor increased linearly with increasing moisture content. Measurements on biomass and bentonite mixtures show a quadratic increase in dielectric constant and loss factor with increasing bentonite content and with moisture contents ranging from 9.5% (pure bentonite) to 11.4% (pure biomass) wet basis. At 915 MHz, dielectric constant ranged from 2.0 to 6.2 and dielectric loss ranged from 0.2 to 2.7 respectively. At 2450 MHz, dielectric constant ranged from, 1.8 to 5.1, and dielectric loss ranged from 0.7 to 2.6, respectively.

KEYWORDS: bentonite; dielectric properties; biomass; microwave absorber; bioenergy

1. INTRODUCTION

Lignocellulosic biomass is an abundant energy resource that can be converted into high energy products via pyrolysis. Pyrolysis is carried out in an inert environment at temperatures of 450- 900°C. At these conditions, the biomass thermochemically decomposes via depolymerization and fragmentation of hemicellulose, cellulose, and lignin to produce condensable gases (bio-oil), non-condensable gases, and biochar. Conventional pyrolysis is typically conducted in reactors such as fixed-bed reactors, fluidized bed reactors, ablative reactors, and rotating cone reactors [1]. These rely on heating by conduction and convection, which results in energy losses to the surrounding environment and losses to the heat transfer medium (fluidized bed and/or the reactor wall). More efficient heating can be attained by utilization of microwave heating for pyrolysis to volumetrically heat the biomass material to pyrolysis temperatures [2]. Moreover, microwave pyrolysis has been found to reduce secondary reactions of the evolved gases compared to conventional pyrolysis, leading to the formation of more desirable products [3, 4]. While utilization of microwave heating for pyrolysis is the subject of many recent studies, only a few studies have characterized the dielectric properties of pyrolysis feedstock materials, which are of paramount importance in design and optimization of microwave processes [5-7].

In order to effectively utilize microwave heating for pyrolysis, it is important to understand the coupling of microwaves with the dielectric material to be heated, which can be accomplished by measurement of material dielectric properties. Dielectric materials are defined as electrical insulators that are polarizable in an applied electric field, and at microwave frequencies, dipole and ionic polarization are dominant. In the case of organic materials, such as biomass feedstocks used for pyrolysis, both types of polarization occur. Bound and free water in

the material undergoes dipole polarization, while the electric potential of membranes within cells of biological tissue undergo ionic polarization [8]. Thus, the water content and composition of the material are important factors in the coupling of microwave energy with biomass materials.

Knowledge of dielectric properties provide information about the specific interaction of dielectric materials with an applied electric field. Dielectric properties are commonly described by the complex relative permittivity, which is expressed by $\epsilon^* = \epsilon' - j\epsilon''$, where the dielectric constant (ϵ') is the real part, the dielectric loss factor (ϵ'') is the imaginary part, and $j = \sqrt{-1}$ [9]. The dielectric constant describes the ability of the material to store energy and the dielectric loss factor describes the ability of the material to dissipate energy.

Pyrolysis feedstocks such as dry lignocellulosic biomass are largely transparent to microwaves, thus only a small percent of the microwave energy is transferred to the biomass material and converted to heat [10]. Poor heating efficiency due to low-loss feedstocks can be remediated by addition of a microwave absorber, a material that is susceptible to microwave heating [11]. Microwave absorbers are widely added to the bulk material to accelerate heating processes, including pyrolysis [12-14]. Many microwave absorbers have been investigated for their effect on microwave pyrolysis including carbonaceous materials (biochar, graphene, SiC) [15], inorganic compounds [16], and clays [17]. While carbonaceous materials are the most widely researched in the literature as a microwave absorber for pyrolysis, clays have garnered recent attention as microwave absorbers [17].

Clays are a low cost and abundant microwave absorbing material and some types have been shown to have catalytic properties. Badr et al. studied the effect of K_3PO_4 mixed with clays (clinoptilolite and bentonite) for their microwave absorbing ability and catalytic effect on the pyrolysis products [17]. In their study, mixtures of K_3PO_4 with bentonite were found to have the greatest catalytic effect on the pyrolysis vapors. Bentonite is a naturally occurring sodium montmorillonite clay that is used in industry as a viscosifying agent in petroleum drilling mud and as a filler in many cosmetics. It is characterized by swellable 2:1 silica layers, which readily adsorb water molecules from the environment, high cationic exchange capacity, and has been found to act as a catalyst for several applications, including pyrolysis [17, 18]. Additionally, bentonite has been investigated for its effect on microwave processing due to its susceptibility to microwave heating [19, 20]. Due to its hygroscopic nature, the effect of bentonite moisture content on dielectric properties is important as its moisture content can change significantly during storage, especially in humid environments. As water is highly polar, adsorbed water can greatly influence dielectric properties.

While many studies have researched the effect of microwave absorbers on microwave pyrolysis, there is a scarcity of literature data focused on characterizing the dielectric properties of pyrolysis feedstocks. Knowledge of material dielectric properties can aid in understanding the attenuation of microwave energy through the material during processing. Bentonite dielectric properties have only been studied on bentonite suspensions and on bentonite pastes [19] except for one study which measured dielectric properties of low-moisture bentonite clays at a low frequency range from 10^{-4} to 10^6 MHz for dielectric moisture sensing applications [20]. This study investigates for the first time to our knowledge the dielectric properties of low-moisture bentonite in the microwave frequency range. In this study, dielectric measurements were made on bentonite at various moisture contents from 0.5 to 4.5 GHz and on mixtures of bentonite with lignocellulosic biomass from 0.5 to 20 GHz. These frequency ranges are significant as they

cover the two most commonly used frequencies for dielectric heating (915 and 2450 MHz), which are designated by the Federal Communications Commission for industrial, scientific, and medical applications.

The biomasses utilized in this study were chosen based on regional availability and potential as waste biomass feedstocks for pyrolysis. Chinese tallow tree is an undesirable invasive species in the Southeastern United States and could provide a vast source of waste biomass [21, 22]. Energy cane is a variety of sugarcane that is modified to produce greater lignocellulosic biomass yields. Energy cane bagasse was used in this study, which is the residual lignocellulosic biomass that remains after pressing the juices from the cane and it was shown to produce bio-oil via pyrolysis [21]. Pine sawdust is a waste product from many forestry and milling operations, which make it a plentiful lignocellulosic waste [23]. Finally, switchgrass is a grassy energy crop, which is characterized by its rapid growth and high biomass yield [23].

2. MATERIALS AND METHODS

2.1. Sample preparation

Initial moisture contents of the bentonite samples were determined by oven drying. Four saturated salt solutions were prepared in jars with airtight lids to produce environments of different relative humidity inside each jar. The prepared saturated salt solutions were K_2SO_4 , KCl, K_2CO_3 , and LiCl, which resulted in relative humidities of 97.5, 85.11, 43.16, and 11.31%, respectively. Vials containing bentonite samples of known weight and initial moisture content were placed into each jar and elevated above a solution of saturated salt. The samples remained in the jars for three weeks until absorption of water vapor by the bentonite samples reached equilibrium, then moisture contents of the bentonite samples were determined on a wet basis ($MC_g = \frac{m_{Water}}{m_{Water} + m_{Bentonite}}$). The obtained bentonite moisture contents and gravimetric bulk densities are presented in Table 1.

Table 1: Saturated salt solution and the resulting bentonite properties

Saturated Salt	Relative humidity (%)	Bentonite moisture content (% w.b.)	Bulk density* (g/cm ³)
K_2SO_4	97.59	18.37	1.31
KCl	85.11	13.56	1.24
K_2CO_3	43.16	6.62	1.16
LiCl	11.31	2.38	1.11

*compressed with about 25 N

Biomass and bentonite mixtures were also prepared for measurement. Biomass samples from pine, Chinese tallow tree, energy cane, and switchgrass were milled and sieved to $< 500 \mu m$ diameter and mixed with powdered bentonite to create mixtures of 0, 25, 50, 75, and 100 weight percent bentonite. Moisture content of each sample was determined according to ASTM E871-

82. Moisture content and bulk density at the time of measurement are presented in Table 2 for each biomass/bentonite mixture.

Table 2: Moisture content and density* of each measured biomass/bentonite mixture.

Bentonite (% wt)	Chinese Tallow Tree		Energy cane		Pine sawdust		Switchgrass	
	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)
0	11.36 ± 0.07	0.33	10.02 ± 0.13	0.19	11.37 ± 0.17	0.37	11.37 ± 0.80	0.25
25	10.89 ± 0.05	0.45	9.88 ± 0.10	0.22	10.89 ± 0.13	0.45	10.89 ± 0.60	0.33
50	10.41 ± 0.04	0.59	9.74 ± 0.07	0.33	10.41 ± 0.08	0.56	10.42 ± 0.40	0.43
75	9.94 ± 0.02	0.73	9.60 ± 0.04	0.54	9.94 ± 0.04	0.68	9.94 ± 0.50	0.64
100	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94

*compressed with about 5 N

2.2. Permittivity measurements of bentonite at different moisture contents

Dielectric properties are strongly correlated to moisture content. Due to the affinity of bentonite clays to absorb water from the atmosphere, the dielectric properties of bentonite at various moisture contents were measured to determine the effect of adsorbed water. The measurement setup consisted of a vector network analyzer (Agilent E5071C), open-ended coaxial-line dielectric probe, and Agilent 85070 measurement software. Calibration consisted of measurements of open air, a short, and 25 °C deionized water according to the manufacturer's recommendation (Agilent Technologies). Samples were packed into a cylindrical stainless-steel cup (2 cm x 2 cm), filled to volume, and placed on a laboratory jack. Bulk density of each sample was determined by dividing the sample mass by the sample holder volume. The dielectric probe was fixed on a stand and the laboratory jack was raised until firm contact was made between the sample and the probe. Dielectric properties were measured immediately after removing the bentonite samples from the controlled humidity jars to minimize changes in moisture content between sample preparation and measurement. Permittivity was measured from 0.5 to 4.5 GHz at 101 linear frequency points and each sample was measured in triplicate. Between each replicate, the sample was agitated and repacked into the sample holder to ensure consistency of measurements and to average out any inhomogeneities in the sample.

2.3. Permittivity measurements of biomass/bentonite mixtures

In this study, dielectric constant and dielectric loss factor of biomass and bentonite mixtures were measured from 500 MHz to 20 GHz. The measurement procedure is similar to that used for the pure bentonite samples at different moisture contents with the following exceptions: an Agilent N5230C PNA-L vector network analyzer was utilized for taking measurements, which collected permittivity data over a 101 point logarithmic frequency sweep from 500 MHz to 20 GHz.

2.4. Density correction method

Dielectric permittivity is dependent on bulk density of the measured material. Several models have been established to describe the correlation of permittivity with bulk density including the complex refractive index (CRI), Lifshitz, Landau, Looyenga (LLL) equation, Böttcher, Buggement-Hanai, Rayleigh, and Lichtenecker. Nelson (1992) found the LLL equation to be the most reliable mixture equation for correlating the material bulk density to the medium density for granular materials [24]. As such, the LLL equation was used in this study to correct the measured permittivity for changes in bulk density and is expressed as:

$$\varepsilon_2' = \left[\frac{\varepsilon_1^{1/3} - 1}{\rho_1} \rho_2 + 1 \right]^3, \quad [1]$$

where ε is the permittivity of the material at density ρ and the subscripts 1 and 2 denote the two states of the material. The LLL equation was utilized to convert the measured permittivities to density-corrected permittivities at each frequency of interest.

3. RESULTS AND DISCUSSION

3.1. Permittivity data of bentonite at different moisture contents

Dielectric constant and dielectric loss factor of bentonite were measured at various water contents in the microwave frequency range from 0.5 to 4.5 GHz. In this range, both dielectric constant and dielectric loss factor decrease monotonically with frequency (Figure 1). For the bentonite moisture contents studied, dielectric constant ranges from 3.0 to 17.0 while dielectric loss factor ranges from 0.8 to 14.7. There is an evident trend of increasing permittivity with increasing moisture content.

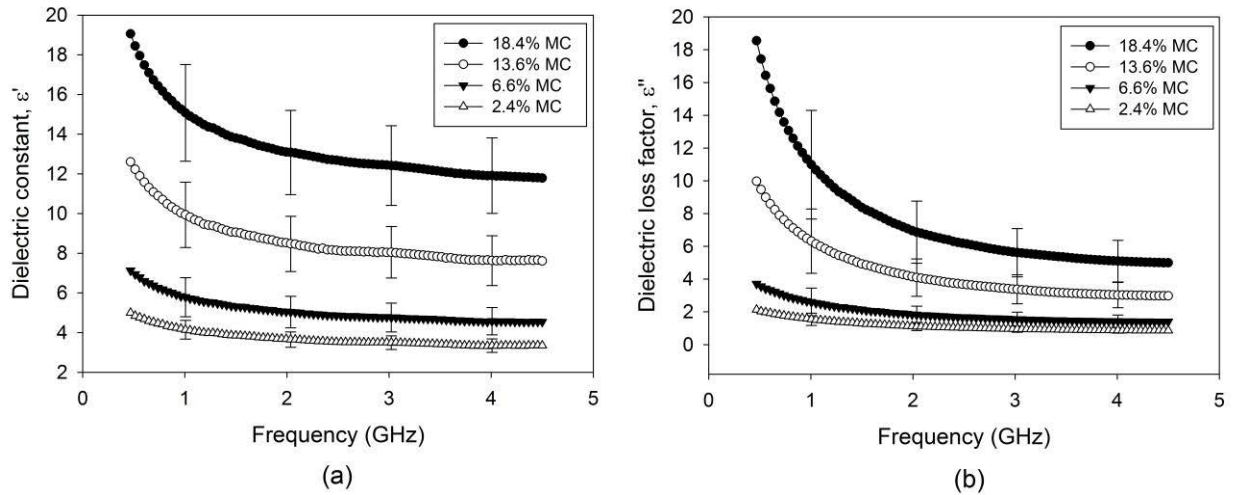


Figure 1: (a) Dielectric constant and (b) dielectric loss factor as a function of frequency from 0.5 to 4.5 GHz at various moisture contents. Error bars indicate standard deviations.

As dielectric properties are a function of the volumetric composition, the dependence of permittivity with moisture content is shown by plotting permittivity as a function of volumetric moisture content at a single frequency (Figure 2). The LLL equation was used to adjust the measured permittivity data for changes in density at different moisture contents. The mean density of 1.2 g/cm^3 was used for this purpose. The correlations between dielectric properties and moisture content are described by a linear regression, which is consistent with the literature [20, 25, 26]. The relative permittivity of deionized water at room temperature and 2450 MHz is 81 as it is a polar molecule that has a high polarization intensity in a time-varying electric field, thus the dielectric properties of solids are strongly affected by moisture content. With increasing water content, the effective dielectric permittivity of bentonite increases. The water in the bentonite is bound water as the saturation point of bentonite is greater than the moisture contents tested. Water is bound to the solid matrix of the bentonite restricting its mobility and by extension, reducing its ability to polarize. This is reflected in a decrease in complex permittivity compared to free water.

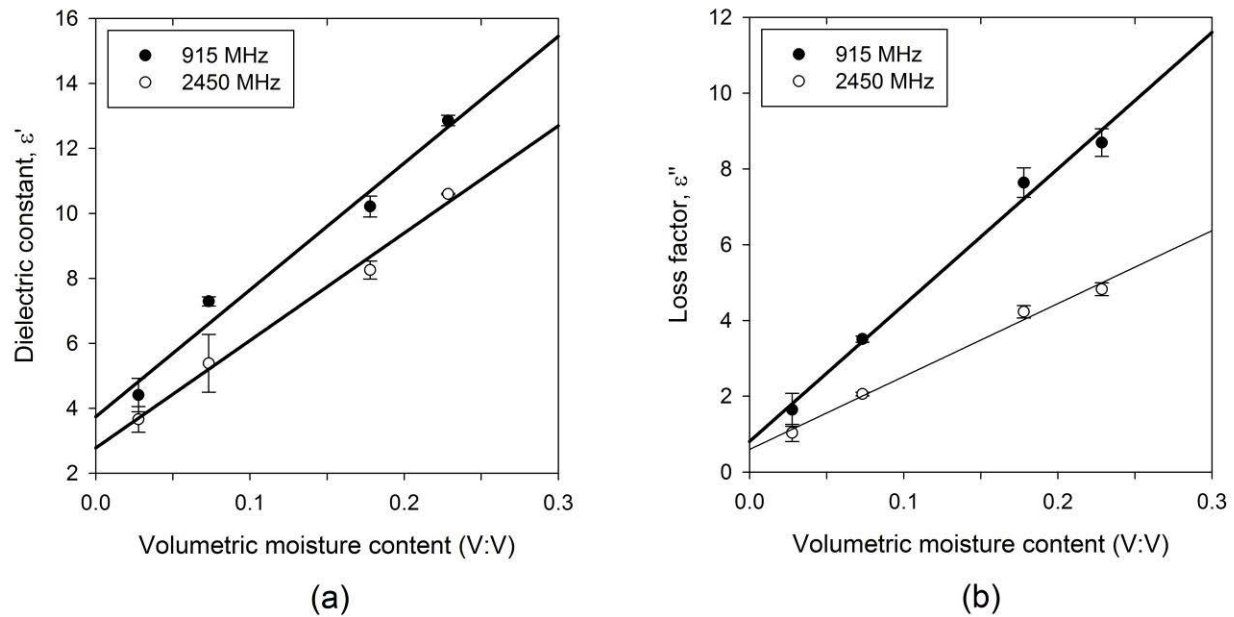


Figure 2: (a) Dielectric constant and (b) dielectric loss factor as a function of volumetric moisture content at 2.45 GHz. Permittivity values were adjusted to the mean bulk density ($\rho = 1.2 \text{ g/cm}^3$) by the LLL equation. Error bars indicate standard deviations.

3.2. Permittivity data of biomass/bentonite mixtures

Permittivity measurements were obtained for various biomass and bentonite mixtures at room temperature from 0.5 to 20 GHz and the effects of bentonite content on dielectric constant are presented as a function of frequency for each biomass in Figure 3. Dielectric constant decreased over the measured frequency range for all mixtures. All of the biomasses measured were found to have similar dielectric constants, whereas bentonite was found to have a greater dielectric constant. Dielectric constant ranged from 1.67 to 2.02 for CTT, 1.42 to 1.70 for energy

cane, 2.05 to 2.70 for pine sawdust, 1.63 to 1.92 for switchgrass, and 3.81 to 7.13 for bentonite. With the addition of bentonite to biomass, an increase in dielectric constant is observed. The same general trend is observed for dielectric loss factor of biomass and bentonite mixtures (Figure 3b). Loss factor ranges from 0.13 to 0.15 for CTT, 0.07 to 0.13 for energy cane, 0.32 to 0.34 for pine sawdust, 0.13 to 0.21 for switchgrass, and 1.02 to 3.78 for bentonite.

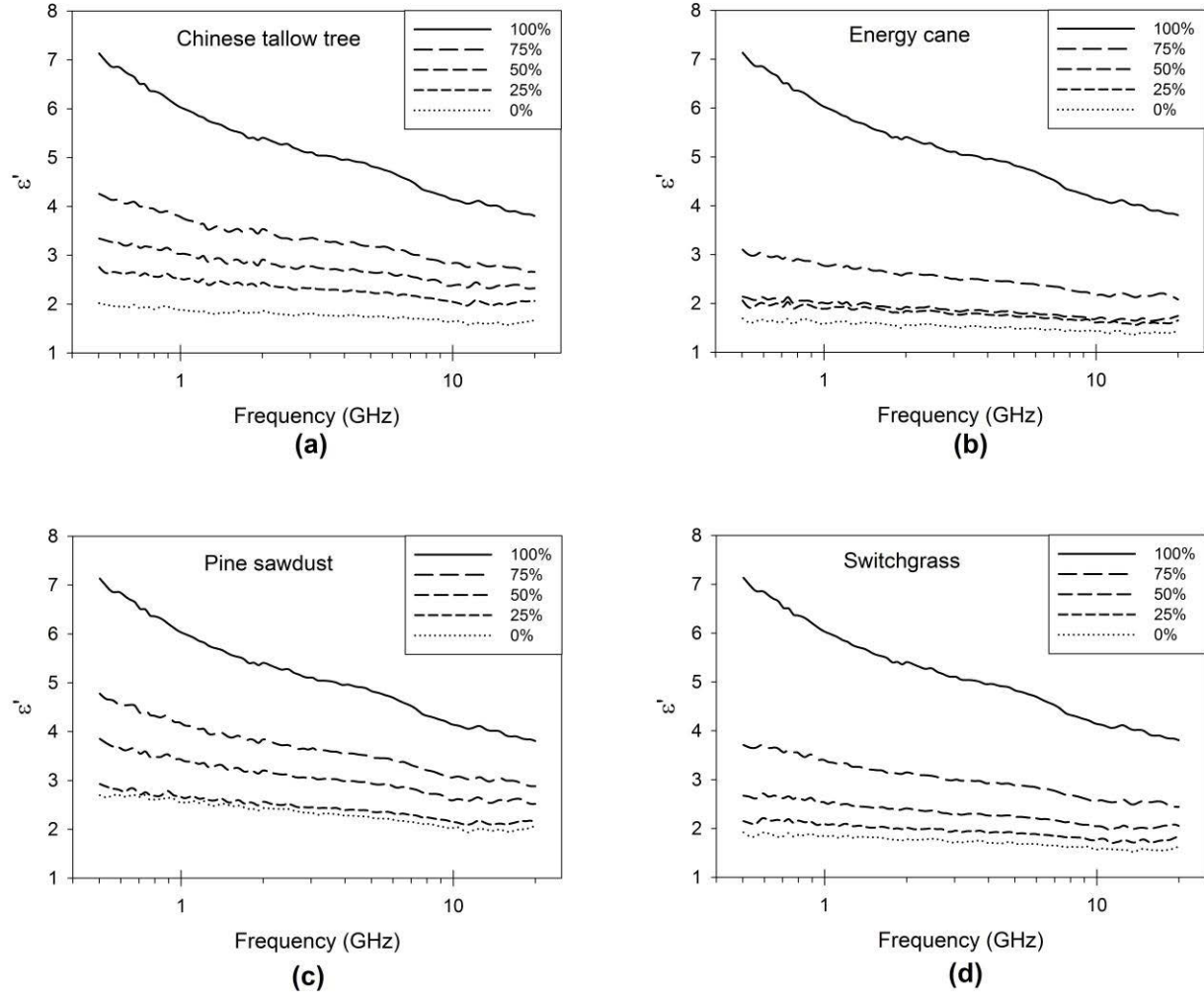


Figure 3: Measured dielectric constant as a function of frequency from 0.5 to 20 GHz for mixtures of bentonite with each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, and (d) switchgrass. Legend indicates percent bentonite.

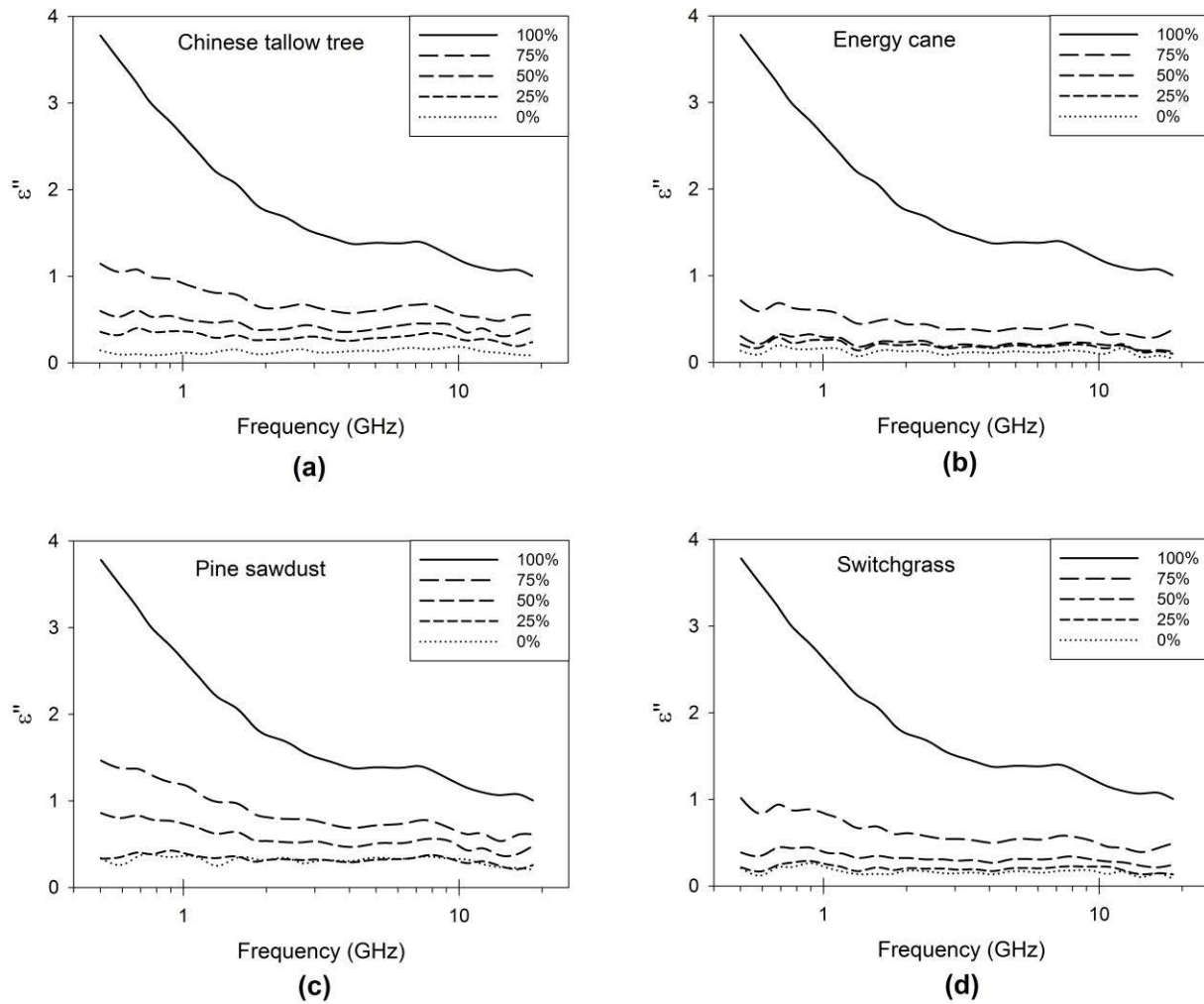


Figure 4: Measured dielectric loss factor as a function of frequency from 0.5 to 20 GHz for mixtures of bentonite with each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, and (d) switchgrass. Legend indicates percent bentonite.

A peak in dielectric loss factor is observed at 8 GHz indicating a Debye-like dielectric relaxation, which is more prominent with greater bentonite content. Such a relaxation is likely due to a combination of interfacial polarization and bound water polarization at this frequency. Smectite clays, such as bentonites, are aggregates of lamellar layers with interlamellar adsorbed water. The surfaces of the layers are charged creating a charge separation between the layers, which are polarizable under the influence of an electric field. Further, the bound water is polarizable, however less so than free water. Free water has a specific dielectric relaxation around 17 GHz at room temperature, while the relaxation frequency observed in our measurements of bentonite is only 8 GHz. This is due to the restricted mobility of water molecules that are adsorbed to the bentonite. Finally, a sharp decrease in dielectric loss factor is seen at the lower region of the frequency spectrum and is most evident for measurements on pure

bentonite samples. This feature is indicative of ionic polarization effects, which is likely due to the charge separation between the lamellar layers.

Dielectric properties showed a better correlation with bentonite content expressed volumetrically rather than gravimetrically. Thus, dielectric constant and dielectric loss factor at 2.45 GHz are plotted as a function of volumetric bentonite content for each biomass in Figure 5. A quadratic increase in both dielectric constant and dielectric loss factor are observed for all biomasses with increasing bentonite content. Due to the greater dielectric constant and loss factor of bentonite, the effective permittivity of the biomass/bentonite mixture increases with increasing bentonite content according to a quadratic function of the form $y = Ax^2 + Bx + C$. Quadratic regression coefficients are presented in Table 3 for dielectric constant and dielectric loss factor of each biomass studied.

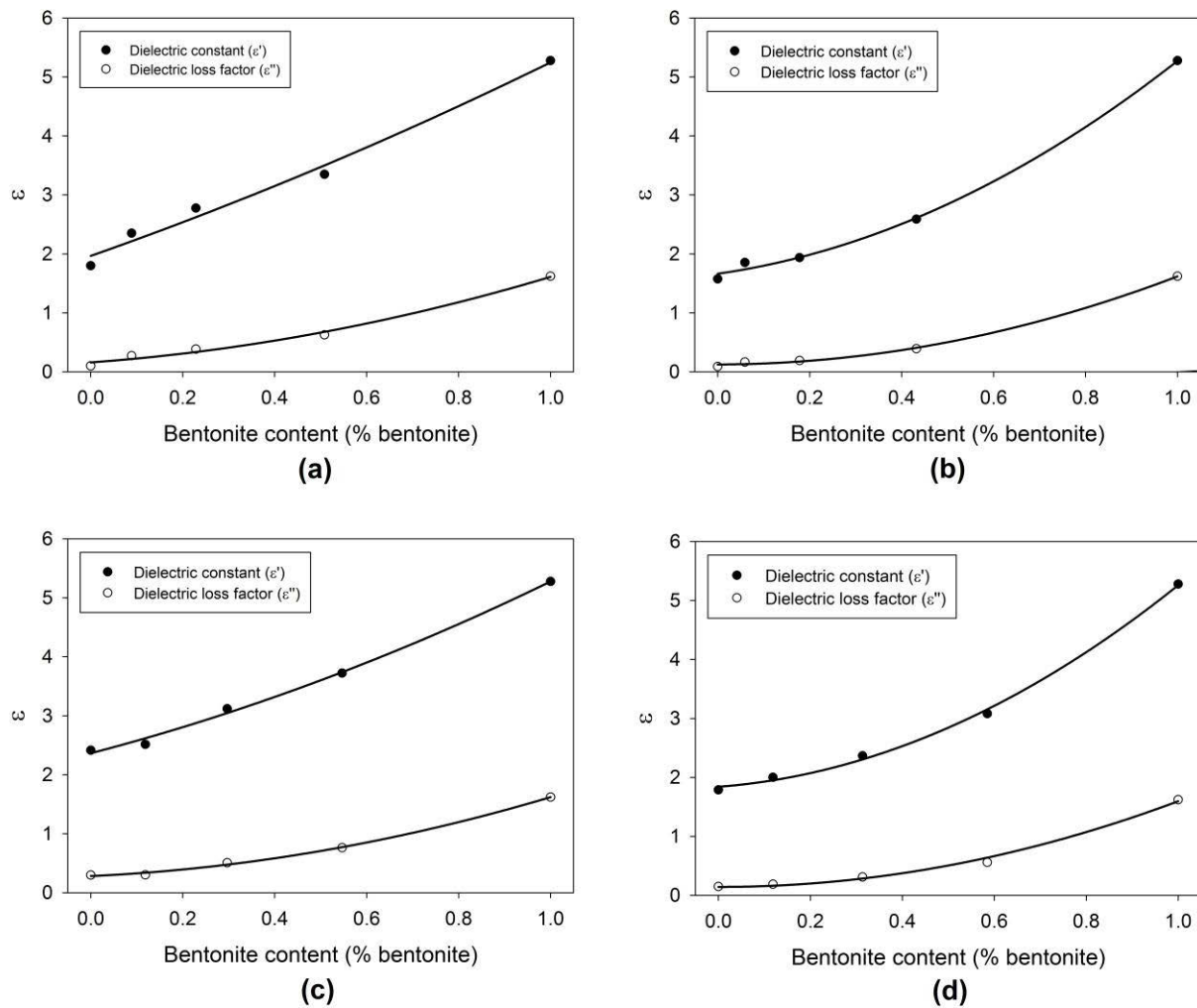


Figure 5: Dielectric constant and dielectric loss factor as a function of volumetric bentonite content for each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, (d) switchgrass.

Table 3: Quadratic regression coefficients for ϵ' and ϵ'' as a function of bentonite content ($y = Ax^2 + Bx + C$)

	ϵ'				ϵ''			
	A	B	C	R ²	A	B	C	R ²
Tallow tree	0.536	2.75	1.97	0.987	0.879	0.571	0.161	0.992
Energy cane	2.50	1.11	1.65	0.998	1.48	1.72	0.126	0.998
Pine sawdust	0.876	2.04	2.37	0.997	0.973	0.366	0.281	0.998
Switchgrass	2.826	0.593	1.84	0.998	1.45	7.66x10 ⁻¹²	0.142	0.994

In other studies of biphasic materials, where one material exhibits greater dielectric properties than the other, similar trends were found. In a biphasic mixture of β -Ca₂P₂O₇ ceramic mixed with TiO₂, the microwave dielectric properties of the mixture increased quadratically with increasing TiO₂ [27]. In a recent study by our group, dielectric properties of mixtures of biomass with biochar were also correlated by quadratic regression equations [5]. This indicates that our approach to measuring dielectric properties of these materials as well as the correlations developed are consistent with the limited literature data available.

4. CONCLUSION

In this study, dielectric measurements were conducted on bentonite samples at different moisture contents as well as on mixtures of bentonite with several biomasses. Bound water was found to have a significant effect on the dielectric properties of bentonite. Dielectric constant and dielectric loss factor increased linearly with increasing moisture content. This trend is an important consideration for microwave processing of bentonite due to its hygroscopic nature. Bentonite dielectric properties may change during storage due to its tendency to uptake moisture from the atmosphere if care is not taken to sequester it from the environment. This study also found that bentonite is a good microwave absorber for biomass pyrolysis as the dielectric properties of biomass and bentonite mixtures increased quadratically with increasing bentonite content. The dielectric constant and loss factor of bentonite are greater than those of the biomasses studied, thus the effective permittivity of the biomass/bentonite mixtures increase with addition of bentonite. Therefore, bentonite is proven to be a good microwave absorber that can be used to increase electromagnetic heating in low loss materials such as biomass.

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DIELECTRIC CHARACTERIZATION OF BENTONITE CLAY AT VARIOUS MOISTURE CONTENTS AND WITH MIXTURES OF BIOMASS IN THE MIROWAVE SPECTRUM

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ABSTRACT

This study assesses the potential for using bentonite as a microwave absorber for microwave-assisted biomass pyrolysis based on the dielectric properties. Dielectric properties of bentonite at different moisture contents were measured using a coaxial line dielectric probe and vector network analyzer in the microwave frequency range from 0.2 to 4.5 GHz at room temperature. Additionally, dielectric properties of mixtures of bentonite with biomass were measured from 1.5 to 20 GHz. As expected, both dielectric constant and dielectric loss factor increased linearly with increasing moisture content. Measurements on biomass and bentonite mixtures show a quadratic increase in dielectric constant and loss factor with increasing bentonite content and with moisture contents ranging from 9.5% (pure bentonite) to 11.4% (pure biomass) wet basis. At 915 MHz, dielectric constant ranged from 2.0 to 6.2 and dielectric loss ranged from 0.2 to 2.7 respectively. At 2450 MHz, dielectric constant ranged from, 1.8 to 5.1, and dielectric loss ranged from 0.7 to 2.6, respectively.

KEYWORDS: bentonite; dielectric properties; biomass; microwave absorber; bioenergy

1. INTRODUCTION

Lignocellulosic biomass is an abundant energy resource that can be converted into high energy products via pyrolysis. Pyrolysis is carried out in an inert environment at temperatures of 450- 900°C. At these conditions, the biomass thermochemically decomposes via depolymerization and fragmentation of hemicellulose, cellulose, and lignin to produce condensable gases (bio-oil), non-condensable gases, and biochar. Conventional pyrolysis is typically conducted in reactors such as fixed-bed reactors, fluidized bed reactors, ablative reactors, and rotating cone reactors [1]. These rely on heating by conduction and convection, which results in energy losses to the surrounding environment and losses to the heat transfer medium (fluidized bed and/or the reactor wall). More efficient heating can be attained by utilization of microwave heating for pyrolysis to volumetrically heat the biomass material to pyrolysis temperatures [2]. Moreover, microwave pyrolysis has been found to reduce secondary reactions of the evolved gases compared to conventional pyrolysis, leading to the formation of more desirable products [3, 4]. While utilization of microwave heating for pyrolysis is the subject of many recent studies, only a few studies have characterized the dielectric properties of pyrolysis feedstock materials, which are of paramount importance in design and optimization of microwave processes [5-7].

In order to effectively utilize microwave heating for pyrolysis, it is important to understand the coupling of microwaves with the dielectric material to be heated, which can be accomplished by measurement of material dielectric properties. Dielectric materials are defined as electrical insulators that are polarizable in an applied electric field, and at microwave frequencies, dipole and ionic polarization are dominant. In the case of organic materials, such as biomass feedstocks used for pyrolysis, both types of polarization occur. Bound and free water in the material undergoes dipole polarization, while the electric potential of membranes within cells of biological tissue undergo ionic polarization [8]. Thus, the water content and composition of the material are important factors in the coupling of microwave energy with biomass materials.

Knowledge of dielectric properties provide information about the specific interaction of dielectric materials with an applied electric field. Dielectric properties are commonly described by the complex relative permittivity, which is expressed by $\epsilon^* = \epsilon' - j\epsilon''$, where the dielectric constant (ϵ') is the real part, the dielectric loss factor (ϵ'') is the imaginary part, and $j = \sqrt{-1}$ [9]. The dielectric constant describes the ability of the material to store energy and the dielectric loss factor describes the ability of the material to dissipate energy.

Pyrolysis feedstocks such as dry lignocellulosic biomass are largely transparent to microwaves, thus only a small percent of the microwave energy is transferred to the biomass material and converted to heat [10]. Poor heating efficiency due to low-loss feedstocks can be remediated by addition of a microwave absorber, a material that is susceptible to microwave heating [11]. Microwave absorbers are widely added to the bulk material to accelerate heating processes, including pyrolysis [12-14]. Many microwave absorbers have been investigated for their effect on microwave pyrolysis including carbonaceous materials (biochar, graphene, SiC) [15], inorganic compounds [16], and clays [17]. While carbonaceous materials are the most widely researched in the literature as a microwave absorber for pyrolysis, clays have garnered recent attention as microwave absorbers [17].

Clays are a low cost and abundant microwave absorbing material and some types have been shown to have catalytic properties. Badr et al. studied the effect of K_3PO_4 mixed with clays (clinoptilolite and bentonite) for their microwave absorbing ability and catalytic effect on the pyrolysis products [17]. In their study, mixtures of K_3PO_4 with bentonite were found to have the greatest catalytic effect on the pyrolysis vapors. Bentonite is a naturally occurring sodium montmorillonite clay that is used in industry as a viscosifying agent in petroleum drilling mud and as a filler in many cosmetics. It is characterized by swellable 2:1 silica layers, which readily adsorb water molecules from the environment, high cationic exchange capacity, and has been found to act as a catalyst for several applications, including pyrolysis [17, 18]. Additionally, bentonite has been investigated for its effect on microwave processing due to its susceptibility to microwave heating [19, 20]. Due to its hygroscopic nature, the effect of bentonite moisture content on dielectric properties is important as its moisture content can change significantly during storage, especially in humid environments. As water is highly polar, adsorbed water can greatly influence dielectric properties.

While many studies have researched the effect of microwave absorbers on microwave pyrolysis, there is a scarcity of literature data focused on characterizing the dielectric properties of pyrolysis feedstocks. Knowledge of material dielectric properties can aid in understanding the attenuation of microwave energy through the material during processing. Bentonite dielectric properties have only been studied on bentonite suspensions and on bentonite pastes [19] except for one study which measured dielectric properties of low-moisture bentonite clays at a low frequency range from 10^{-4} to 10^6 MHz for dielectric moisture sensing applications [20]. This study investigates for the first time to our knowledge the dielectric properties of low-moisture bentonite in the microwave frequency range. In this study, dielectric measurements were made on bentonite at various moisture contents from 0.5 to 4.5 GHz and on mixtures of bentonite with lignocellulosic biomass from 0.5 to 20 GHz. These frequency ranges are significant as they cover the two most commonly used frequencies for dielectric heating (915 and 2450 MHz), which are designated by the Federal Communications Commission for industrial, scientific, and medical applications.

The biomasses utilized in this study were chosen based on regional availability and potential as waste biomass feedstocks for pyrolysis. Chinese tallow tree is an undesirable invasive species in the Southeastern United States and could provide a vast source of waste biomass [21, 22]. Energy cane is a variety of sugarcane that is modified to produce greater lignocellulosic biomass yields. Energy cane bagasse was used in this study, which is the residual lignocellulosic biomass that remains after pressing the juices from the cane and it was shown to produce bio-oil via pyrolysis [21]. Pine sawdust is a waste product from many forestry and milling operations, which make it a plentiful lignocellulosic waste [23]. Finally, switchgrass is a grassy energy crop, which is characterized by its rapid growth and high biomass yield [23].

2. MATERIALS AND METHODS

2.1. Sample preparation

Initial moisture contents of the bentonite samples were determined by oven drying. Four saturated salt solutions were prepared in jars with airtight lids to produce environments of different relative humidity inside each jar. The prepared saturated salt solutions were K_2SO_4 , KCl , K_2CO_3 , and $LiCl$, which resulted in relative humidities of 97.5, 85.11, 43.16, and 11.31%, respectively. Vials containing bentonite samples of known weight and initial moisture content were placed into each jar and elevated above a solution of saturated salt. The samples remained in the jars for three weeks until absorption of water vapor by the bentonite samples reached equilibrium, then moisture contents of the bentonite samples were determined on a wet basis ($MC_g = \frac{m_{Water}}{m_{Water} + m_{Bentonite}}$). The obtained bentonite moisture contents and gravimetric bulk densities are presented in Table 1.

Table 1: Saturated salt solution and the resulting bentonite properties

Saturated Salt	Relative humidity (%)	Bentonite moisture content (% w.b.)	Bulk density* (g/cm ³)
K_2SO_4	97.59	18.37	1.31
KCl	85.11	13.56	1.24
K_2CO_3	43.16	6.62	1.16
$LiCl$	11.31	2.38	1.11

*compressed with about 25 N

Biomass and bentonite mixtures were also prepared for measurement. Biomass samples from pine, Chinese tallow tree, energy cane, and switchgrass were milled and sieved to < 500 μm diameter and mixed with powdered bentonite to create mixtures of 0, 25, 50, 75, and 100 weight percent bentonite. Moisture content of each sample was determined according to ASTM E871-82. Moisture content and bulk density at the time of measurement are presented in Table 2 for each biomass/bentonite mixture.

Table 2: Moisture content and density* of each measured biomass/bentonite mixture.

Bentonite (% wt)	Chinese Tallow Tree		Energy cane		Pine sawdust		Switchgrass	
	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)
0	11.36 ± 0.07	0.33	10.02 ± 0.13	0.19	11.37 ± 0.17	0.37	11.37 ± 0.80	0.25
25	10.89 ± 0.05	0.45	9.88 ± 0.10	0.22	10.89 ± 0.13	0.45	10.89 ± 0.60	0.33
50	10.41 ± 0.04	0.59	9.74 ± 0.07	0.33	10.41 ± 0.08	0.56	10.42 ± 0.40	0.43
75	9.94 ± 0.02	0.73	9.60 ± 0.04	0.54	9.94 ± 0.04	0.68	9.94 ± 0.50	0.64
100	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94

*compressed with about 5 N

2.2. Permittivity measurements of bentonite at different moisture contents

Dielectric properties are strongly correlated to moisture content. Due to the affinity of bentonite clays to absorb water from the atmosphere, the dielectric properties of bentonite at various moisture contents were measured to determine the effect of adsorbed water. The measurement setup consisted of a vector network analyzer (Agilent E5071C), open-ended coaxial-line dielectric probe, and Agilent 85070 measurement software. Calibration consisted of measurements of open air, a short, and 25 °C deionized water according to the manufacturer's recommendation (Agilent Technologies). Samples were packed into a cylindrical stainless-steel cup (2 cm x 2 cm), filled to volume, and placed on a laboratory jack. Bulk density of each sample was determined by dividing the sample mass by the sample holder volume. The dielectric probe was fixed on a stand and the laboratory jack was raised until firm contact was made between the sample and the probe. Dielectric properties were measured immediately after removing the bentonite samples from the controlled humidity jars to minimize changes in moisture content between sample preparation and measurement. Permittivity was measured from 0.5 to 4.5 GHz at 101 linear frequency points and each sample was measured in triplicate. Between each replicate, the sample was agitated and repacked into the sample holder to ensure consistency of measurements and to average out any inhomogeneities in the sample.

2.3. Permittivity measurements of biomass/bentonite mixtures

In this study, dielectric constant and dielectric loss factor of biomass and bentonite mixtures were measured from 500 MHz to 20 GHz. The measurement procedure is similar to that used for the pure bentonite samples at different moisture contents with the following exceptions: an Agilent N5230C PNA-L vector network analyzer was utilized for taking measurements, which collected permittivity data over a 101 point logarithmic frequency sweep from 500 MHz to 20 GHz.

2.4. Density correction method

Dielectric permittivity is dependent on bulk density of the measured material. Several models have been established to describe the correlation of permittivity with bulk density including the complex refractive index (CRI), Lifshitz, Landau, Looyenga (LLL) equation, Böttcher, Buggement-Hanai, Rayleigh, and Lichtenecker. Nelson (1992) found the LLL equation to be the most reliable mixture equation for correlating the material bulk density to the

medium density for granular materials [24]. As such, the LLL equation was used in this study to correct the measured permittivity for changes in bulk density and is expressed as:

$$\varepsilon_2' = \left[\frac{\varepsilon_1^{1/3} - 1}{\rho_1} \rho_2 + 1 \right]^3, \quad [1]$$

where ε is the permittivity of the material at density ρ and the subscripts 1 and 2 denote the two states of the material. The LLL equation was utilized to convert the measured permittivities to density-corrected permittivities at each frequency of interest.

3. RESULTS AND DISCUSSION

3.1. Permittivity data of bentonite at different moisture contents

Dielectric constant and dielectric loss factor of bentonite were measured at various water contents in the microwave frequency range from 0.5 to 4.5 GHz. In this range, both dielectric constant and dielectric loss factor decrease monotonically with frequency (Figure 1). For the bentonite moisture contents studied, dielectric constant ranges from 3.0 to 17.0 while dielectric loss factor ranges from 0.8 to 14.7. There is an evident trend of increasing permittivity with increasing moisture content.

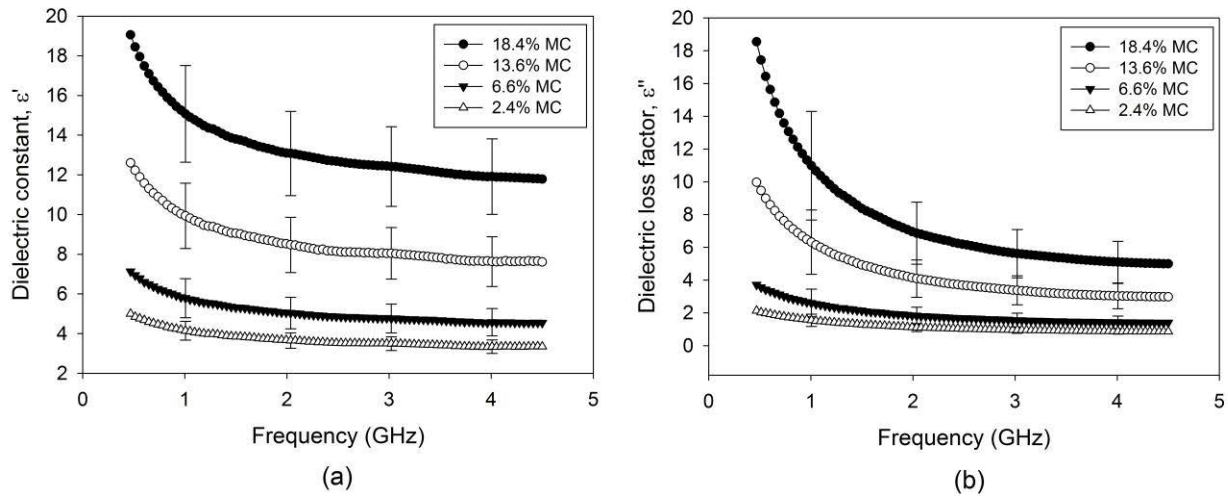


Figure 1: (a) Dielectric constant and (b) dielectric loss factor as a function of frequency from 0.5 to 4.5 GHz at various moisture contents. Error bars indicate standard deviations.

As dielectric properties are a function of the volumetric composition, the dependence of permittivity with moisture content is shown by plotting permittivity as a function of volumetric moisture content at a single frequency (Figure 2). The LLL equation was used to adjust the measured permittivity data for changes in density at different moisture contents. The mean density of 1.2 g/cm³ was used for this purpose. The correlations between dielectric properties and moisture content are described by a linear regression, which is consistent with the literature [20, 25, 26]. The relative permittivity of deionized water at room temperature and 2450 MHz is

81 as it is a polar molecule that has a high polarization intensity in a time-varying electric field, thus the dielectric properties of solids are strongly affected by moisture content. With increasing water content, the effective dielectric permittivity of bentonite increases. The water in the bentonite is bound water as the saturation point of bentonite is greater than the moisture contents tested. Water is bound to the solid matrix of the bentonite restricting its mobility and by extension, reducing its ability to polarize. This is reflected in a decrease in complex permittivity compared to free water.

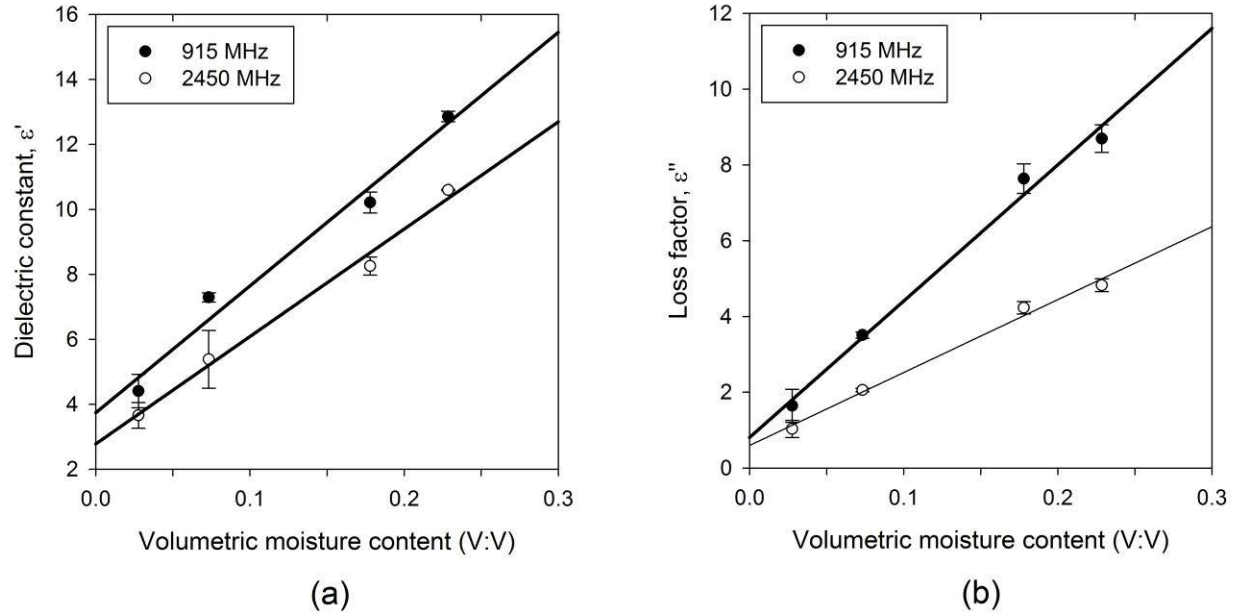


Figure 2: (a) Dielectric constant and (b) dielectric loss factor as a function of volumetric moisture content at 2.45 GHz. Permittivity values were adjusted to the mean bulk density ($\rho = 1.2 \text{ g/cm}^3$) by the LLL equation. Error bars indicate standard deviations.

3.2. Permittivity data of biomass/bentonite mixtures

Permittivity measurements were obtained for various biomass and bentonite mixtures at room temperature from 0.5 to 20 GHz and the effects of bentonite content on dielectric constant are presented as a function of frequency for each biomass in Figure 3. Dielectric constant decreased over the measured frequency range for all mixtures. All of the biomasses measured were found to have similar dielectric constants, whereas bentonite was found to have a greater dielectric constant. Dielectric constant ranged from 1.67 to 2.02 for CTT, 1.42 to 1.70 for energy cane, 2.05 to 2.70 for pine sawdust, 1.63 to 1.92 for switchgrass, and 3.81 to 7.13 for bentonite. With the addition of bentonite to biomass, an increase in dielectric constant is observed. The same general trend is observed for dielectric loss factor of biomass and bentonite mixtures (Figure 3b). Loss factor ranges from 0.13 to 0.15 for CTT, 0.07 to 0.13 for energy cane, 0.32 to 0.34 for pine sawdust, 0.13 to 0.21 for switchgrass, and 1.02 to 3.78 for bentonite.

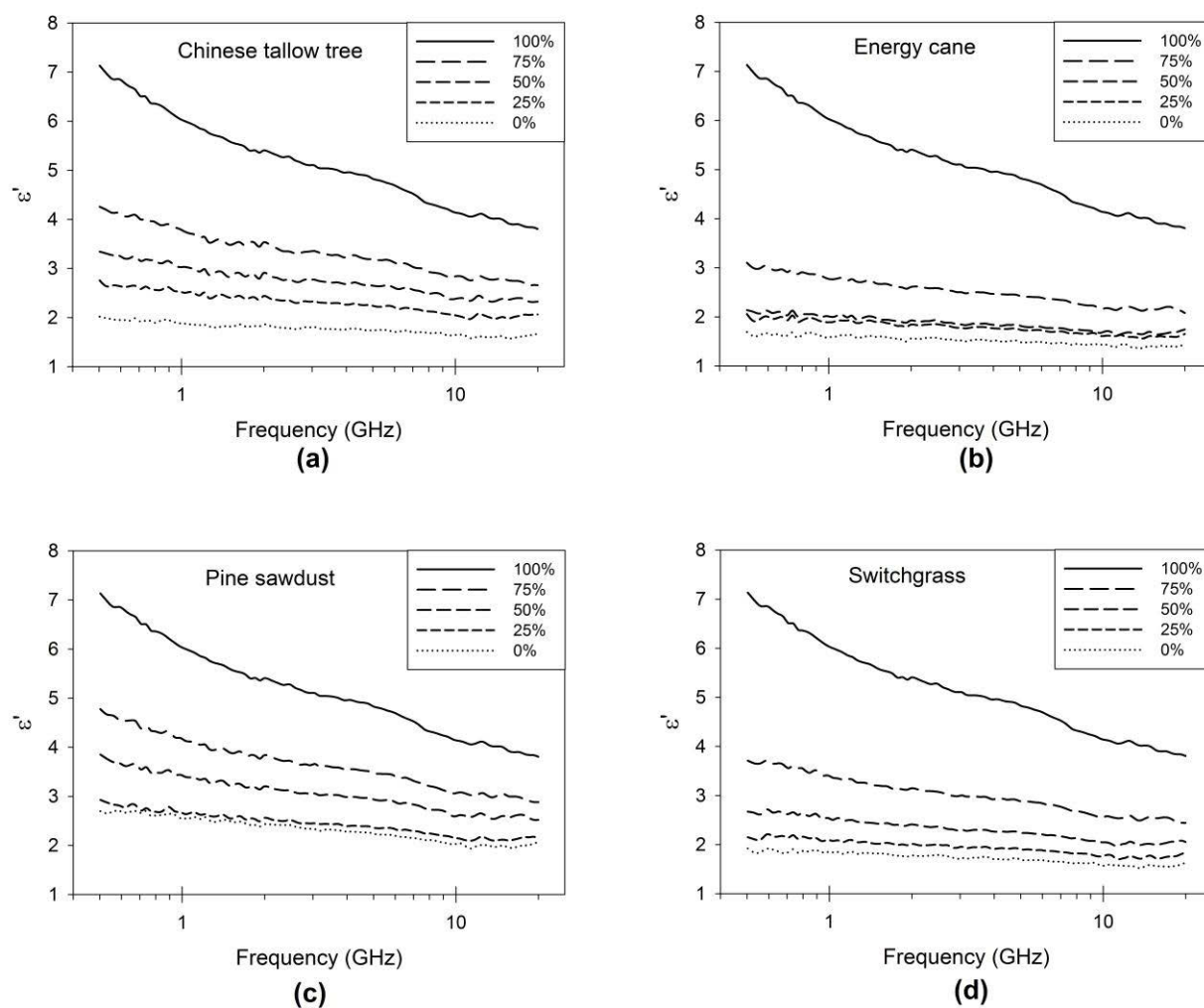


Figure 3: Measured dielectric constant as a function of frequency from 0.5 to 20 GHz for mixtures of bentonite with each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, and (d) switchgrass. Legend indicates percent bentonite.

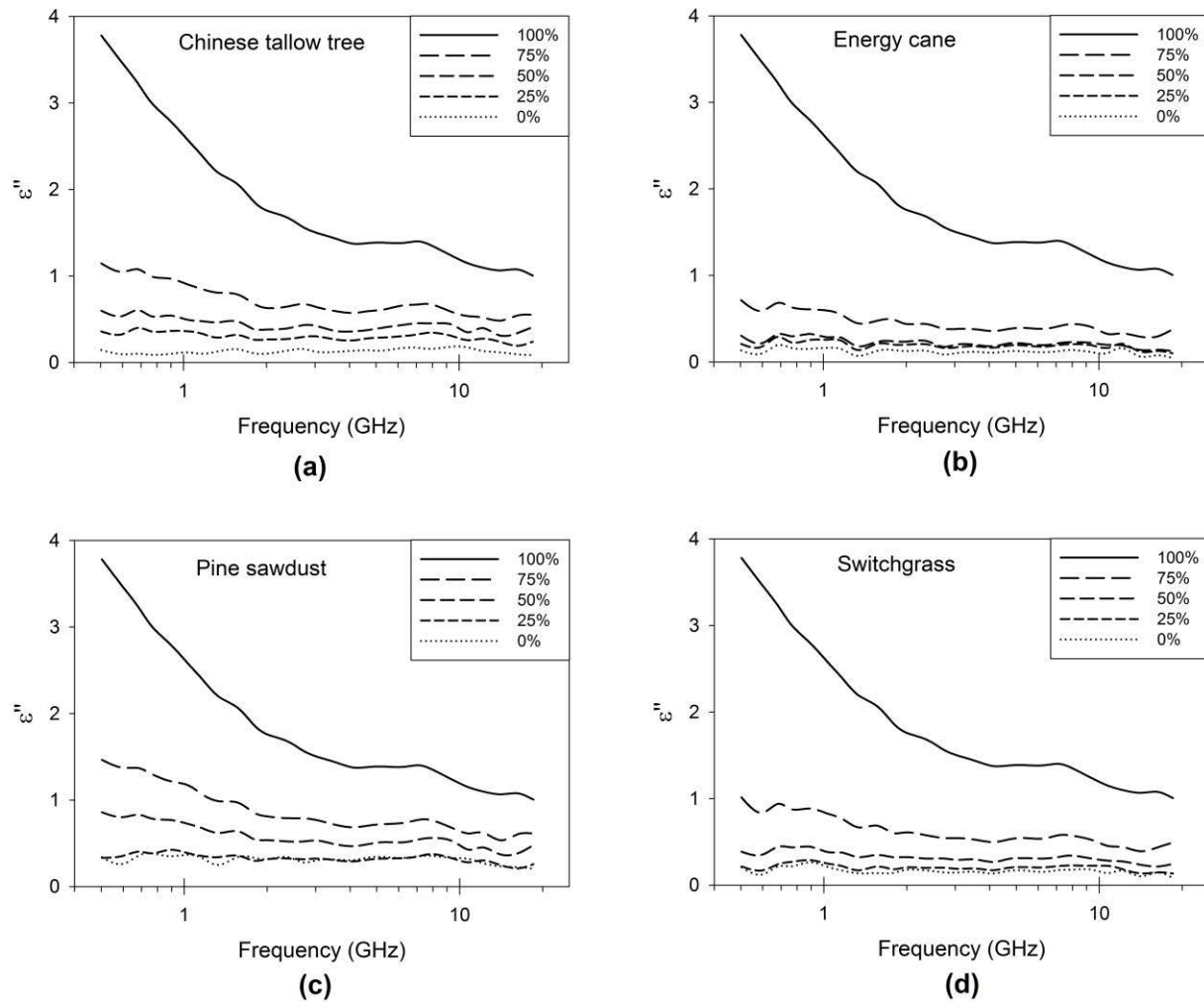


Figure 4: Measured dielectric loss factor as a function of frequency from 0.5 to 20 GHz for mixtures of bentonite with each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, and (d) switchgrass. Legend indicates percent bentonite.

A peak in dielectric loss factor is observed at 8 GHz indicating a Debye-like dielectric relaxation, which is more prominent with greater bentonite content. Such a relaxation is likely due to a combination of interfacial polarization and bound water polarization at this frequency. Smectite clays, such as bentonites, are aggregates of lamellar layers with interlamellar adsorbed water. The surfaces of the layers are charged creating a charge separation between the layers, which are polarizable under the influence of an electric field. Further, the bound water is polarizable, however less so than free water. Free water has a specific dielectric relaxation around 17 GHz at room temperature, while the relaxation frequency observed in our measurements of bentonite is only 8 GHz. This is due to the restricted mobility of water molecules that are adsorbed to the bentonite. Finally, a sharp decrease in dielectric loss factor is seen at the lower region of the frequency spectrum and is most evident for measurements on pure

bentonite samples. This feature is indicative of ionic polarization effects, which is likely due to the charge separation between the lamellar layers.

Dielectric properties showed a better correlation with bentonite content expressed volumetrically rather than gravimetrically. Thus, dielectric constant and dielectric loss factor at 2.45 GHz are plotted as a function of volumetric bentonite content for each biomass in Figure 5. A quadratic increase in both dielectric constant and dielectric loss factor are observed for all biomasses with increasing bentonite content. Due to the greater dielectric constant and loss factor of bentonite, the effective permittivity of the biomass/bentonite mixture increases with increasing bentonite content according to a quadratic function of the form $y = Ax^2 + Bx + C$. Quadratic regression coefficients are presented in Table 3 for dielectric constant and dielectric loss factor of each biomass studied.

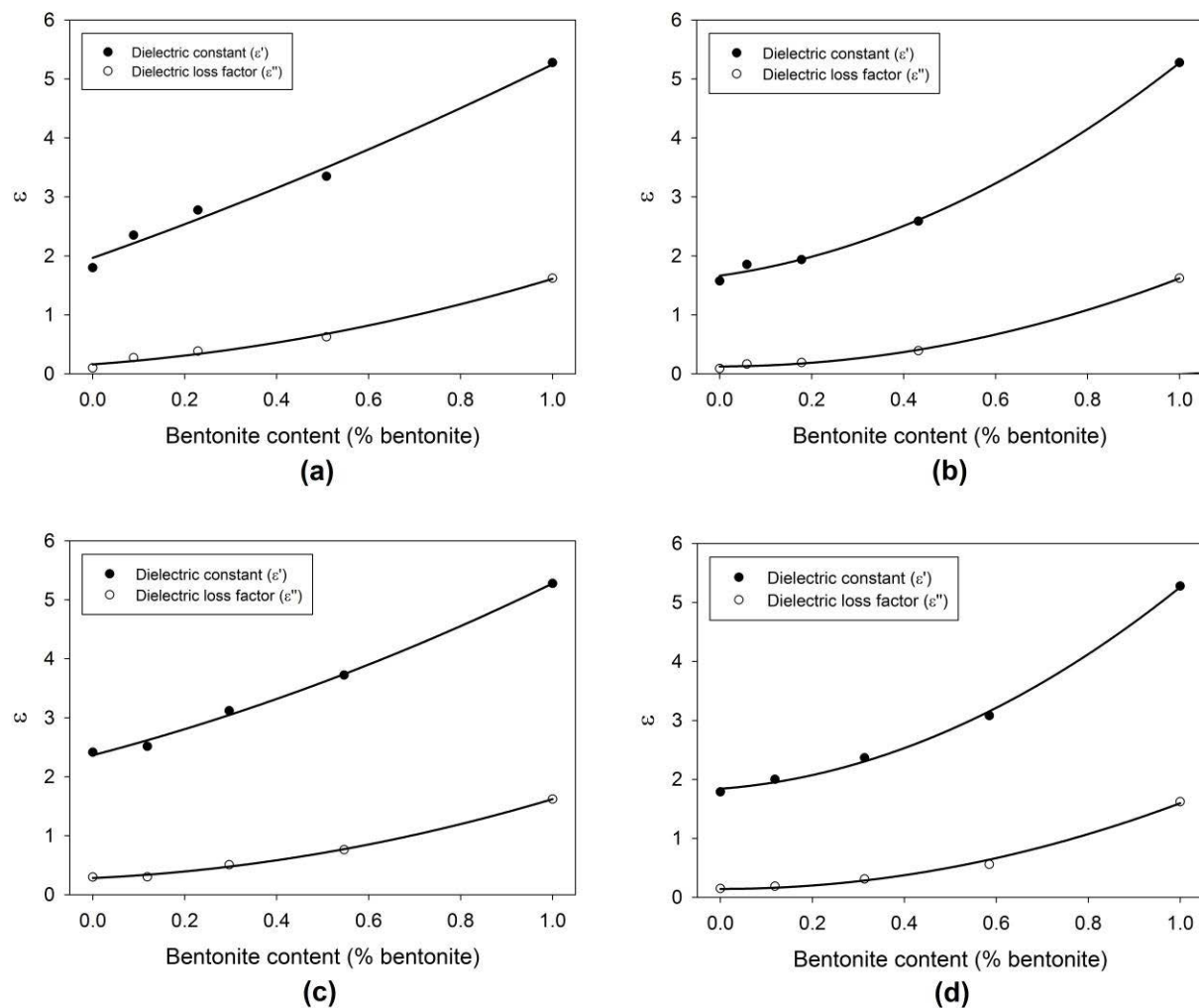


Figure 5: Dielectric constant and dielectric loss factor as a function of volumetric bentonite content for each biomass: (a) Chinese tallow tree, (b) energy cane, (c) pine sawdust, (d) switchgrass.

Table 3: Quadratic regression coefficients for ϵ' and ϵ'' as a function of bentonite content ($y = Ax^2 + Bx + C$)

	ϵ'				ϵ''			
	A	B	C	R ²	A	B	C	R ²
Tallow tree	0.536	2.75	1.97	0.987	0.879	0.571	0.161	0.992
Energy cane	2.50	1.11	1.65	0.998	1.48	1.72	0.126	0.998
Pine sawdust	0.876	2.04	2.37	0.997	0.973	0.366	0.281	0.998
Switchgrass	2.826	0.593	1.84	0.998	1.45	7.66x10 ⁻¹²	0.142	0.994

In other studies of biphasic materials, where one material exhibits greater dielectric properties than the other, similar trends were found. In a biphasic mixture of β -Ca₂P₂O₇ ceramic mixed with TiO₂, the microwave dielectric properties of the mixture increased quadratically with increasing TiO₂ [27]. In a recent study by our group, dielectric properties of mixtures of biomass with biochar were also correlated by quadratic regression equations [5]. This indicates that our approach to measuring dielectric properties of these materials as well as the correlations developed are consistent with the limited literature data available.

4. CONCLUSION

In this study, dielectric measurements were conducted on bentonite samples at different moisture contents as well as on mixtures of bentonite with several biomasses. Bound water was found to have a significant effect on the dielectric properties of bentonite. Dielectric constant and dielectric loss factor increased linearly with increasing moisture content. This trend is an important consideration for microwave processing of bentonite due to its hygroscopic nature. Bentonite dielectric properties may change during storage due to its tendency to uptake moisture from the atmosphere if care is not taken to sequester it from the environment. This study also found that bentonite is a good microwave absorber for biomass pyrolysis as the dielectric properties of biomass and bentonite mixtures increased quadratically with increasing bentonite content. The dielectric constant and loss factor of bentonite are greater than those of the biomasses studied, thus the effective permittivity of the biomass/bentonite mixtures increase with addition of bentonite. Therefore, bentonite is proven to be a good microwave absorber that can be used to increase electromagnetic heating in low loss materials such as biomass.

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P_37_768/schiță: 103651; *Contract no:* 39/02.09.2016. A portion of this work was conducted at and using equipment from the USDA Agriculture Research Service lab in Athens, Georgia. The authors extend their acknowledgement to Pranjali Muley, McKenna Benbow, and Gustavo Aguilar for their technical support. Published with the approval of the Director of the Louisiana Agricultural Experiment Station as manuscript 2017- 232-31418.

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Table 2: Moisture content and density* of each measured biomass/bentonite mixture

Bentonite (% wt)	Chinese Tallow Tree		Energy cane		Pine sawdust		Switchgrass	
	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)	MC (% wet basis)	Density (g/cm ³)
0	11.36 ± 0.07	0.33	10.02 ± 0.13	0.19	11.37 ± 0.17	0.37	11.37 ± 0.80	0.25
25	10.89 ± 0.05	0.45	9.88 ± 0.10	0.22	10.89 ± 0.13	0.45	10.89 ± 0.60	0.33
50	10.41 ± 0.04	0.59	9.74 ± 0.07	0.33	10.41 ± 0.08	0.56	10.42 ± 0.40	0.43
75	9.94 ± 0.02	0.73	9.60 ± 0.04	0.54	9.94 ± 0.04	0.68	9.94 ± 0.50	0.64
100	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94	9.46 ± 0.02	0.94

*compressed with about 5 N

Table 3: Quadratic regression coefficients for ϵ' and ϵ'' as a function of bentonite content ($y = Ax^2 + Bx + C$)

	ϵ'				ϵ''			
	A	B	C	R^2	A	B	C	R^2
Tallow tree	0.536	2.75	1.97	0.987	0.879	0.571	0.161	0.992
Energy cane	2.50	1.11	1.65	0.998	1.48	1.72	0.126	0.998
Pine sawdust	0.876	2.04	2.37	0.997	0.973	0.366	0.281	0.998
Switchgrass	2.826	0.593	1.84	0.998	1.45	7.66×10^{-12}	0.142	0.994

Figure 1

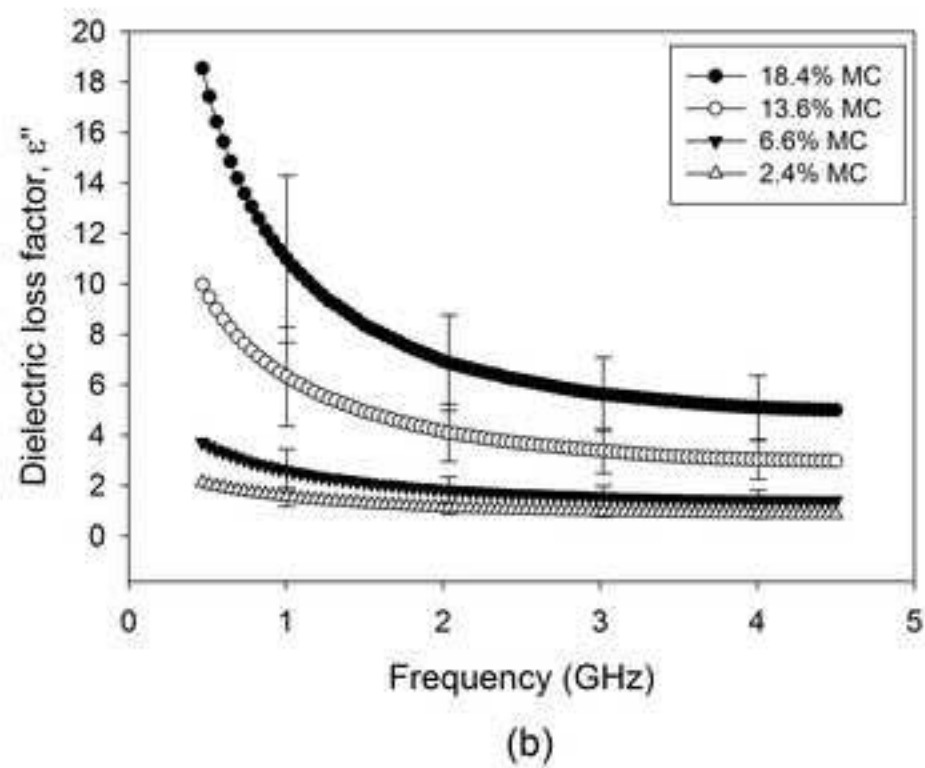
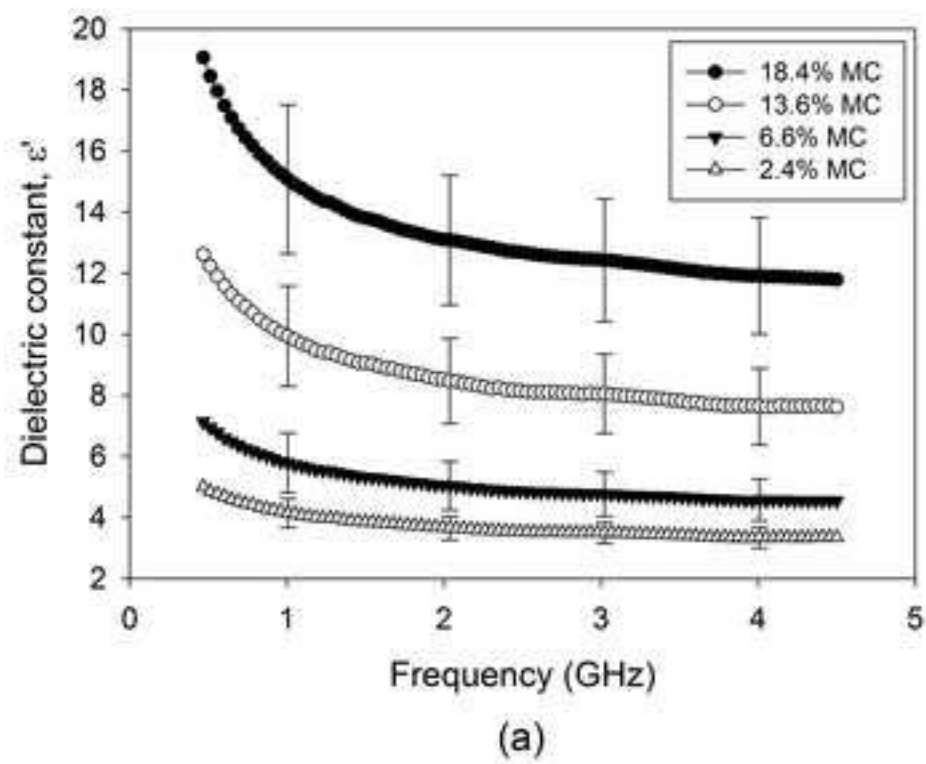
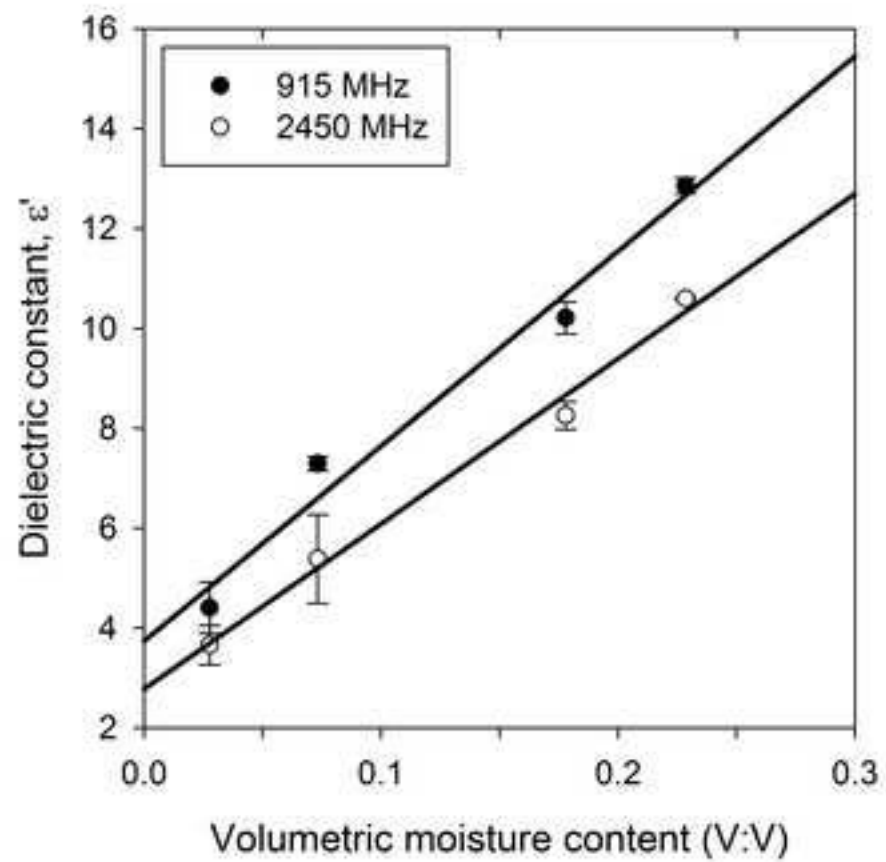
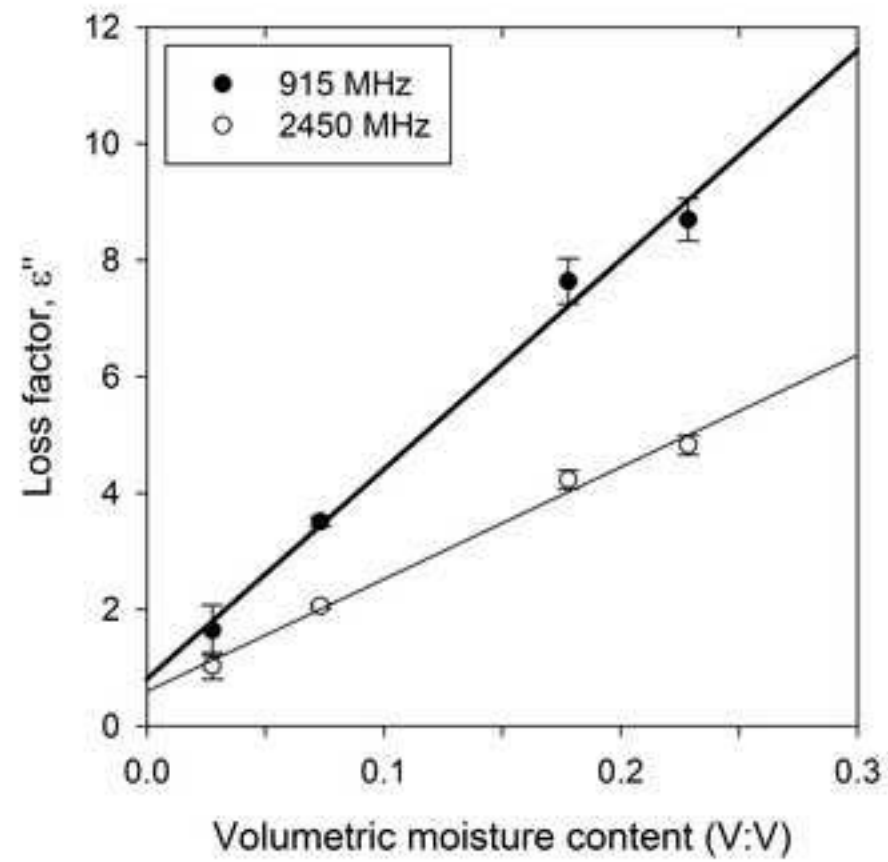


Figure 2



(a)



(b)

Figure 3

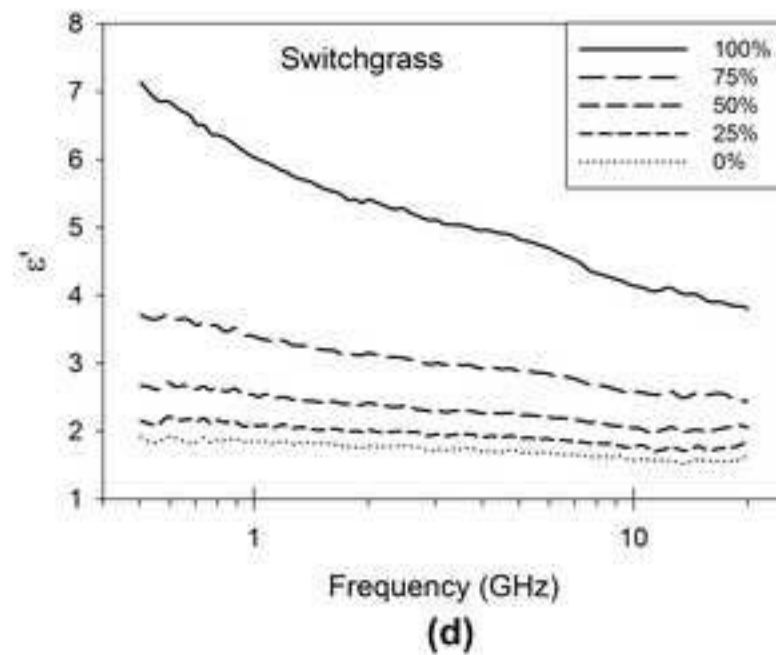
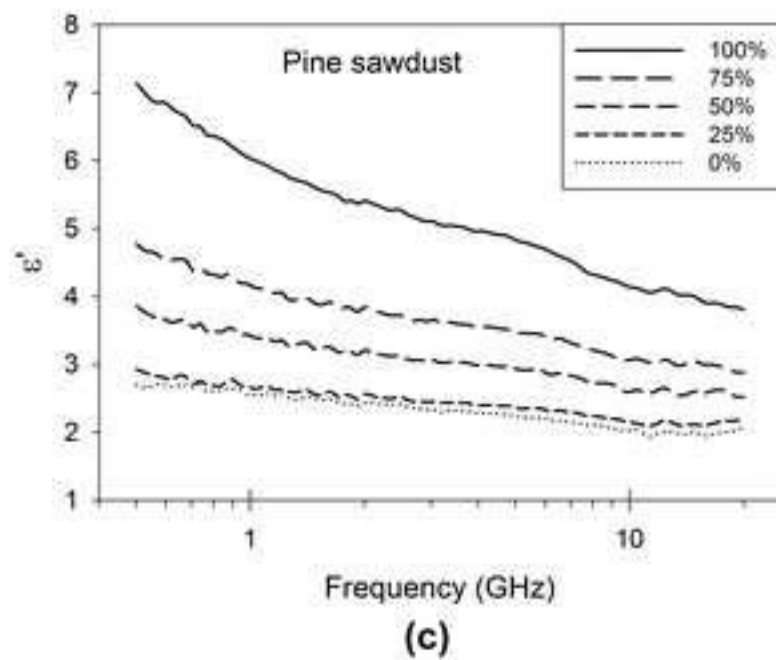
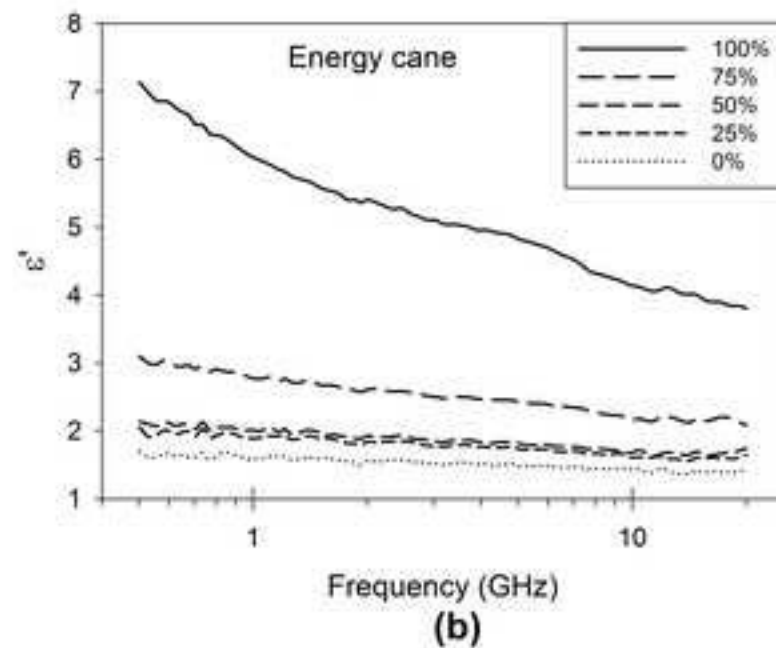
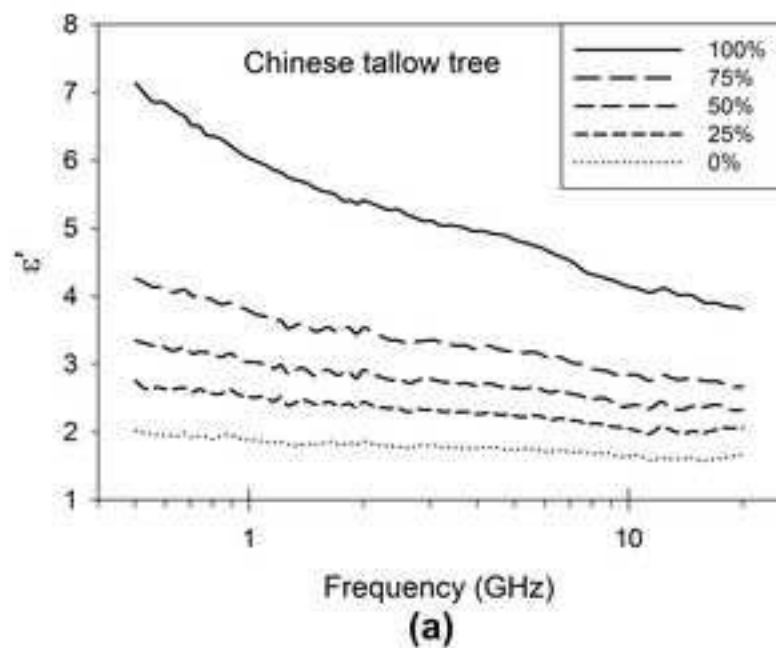
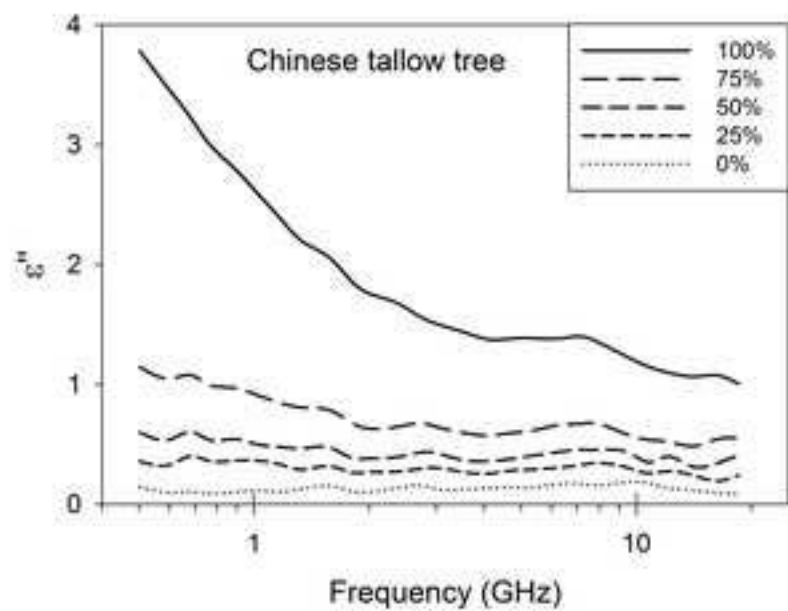
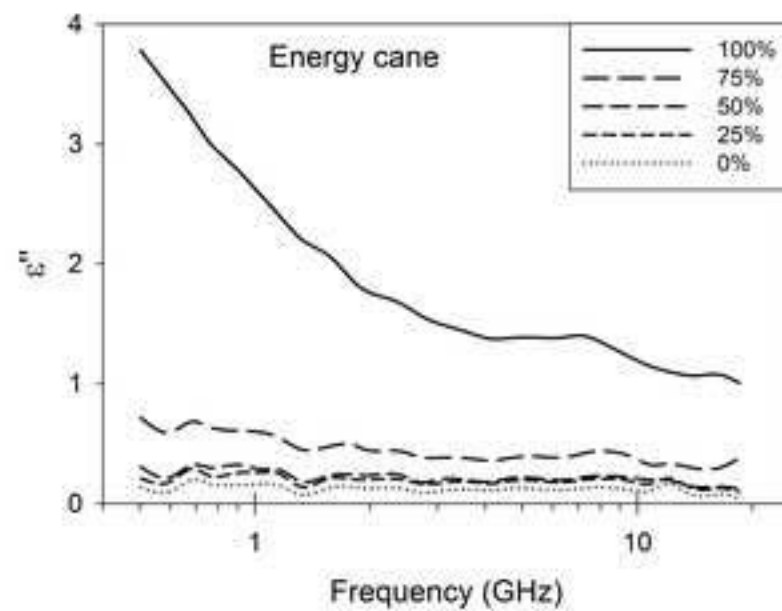


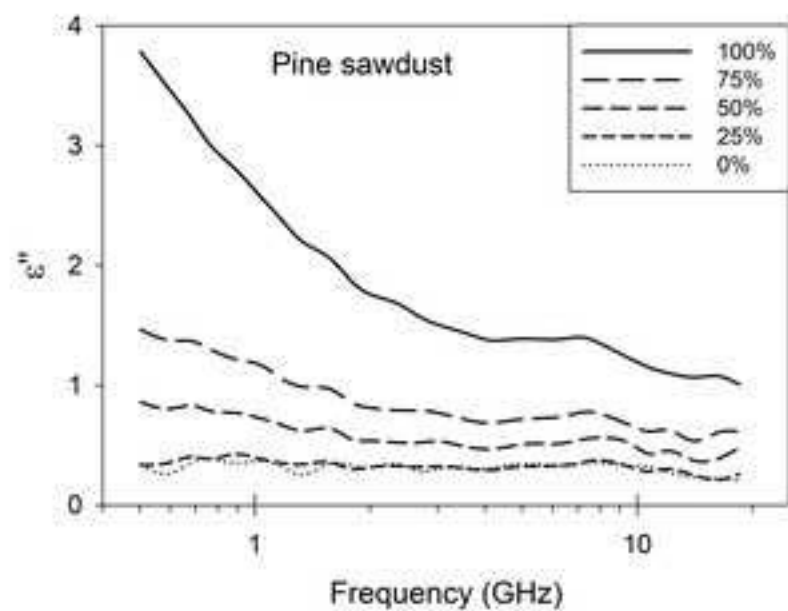
Figure 4



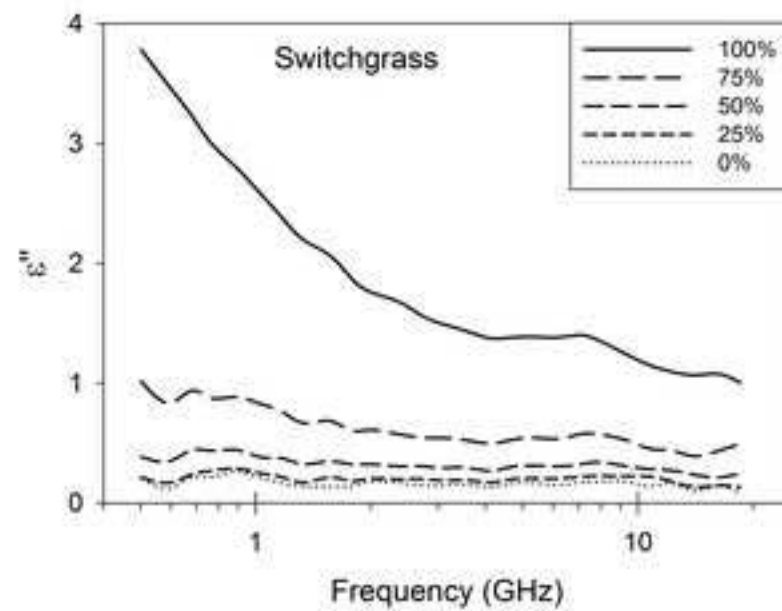
(a)



(b)

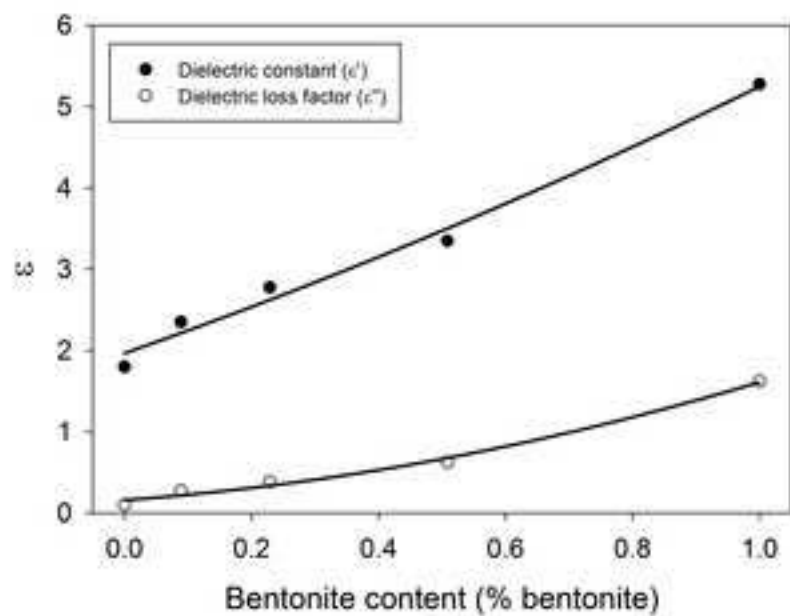


(c)

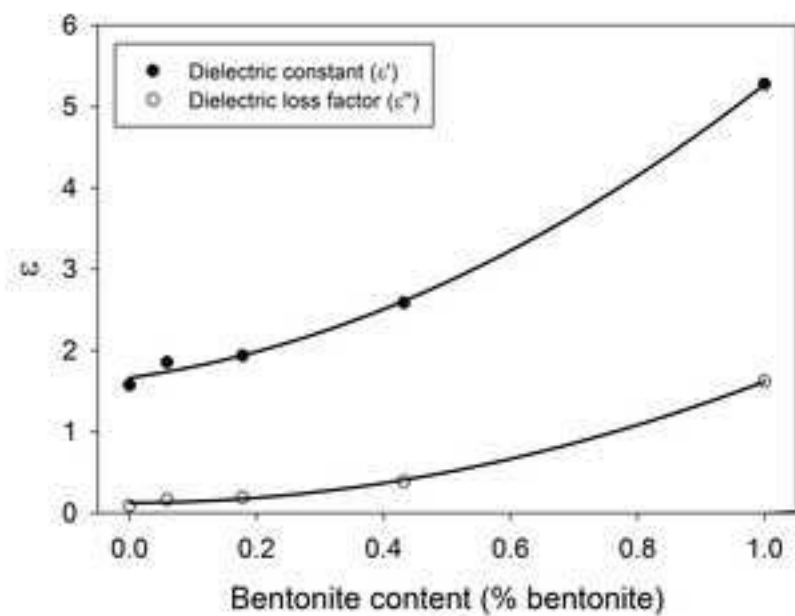


(d)

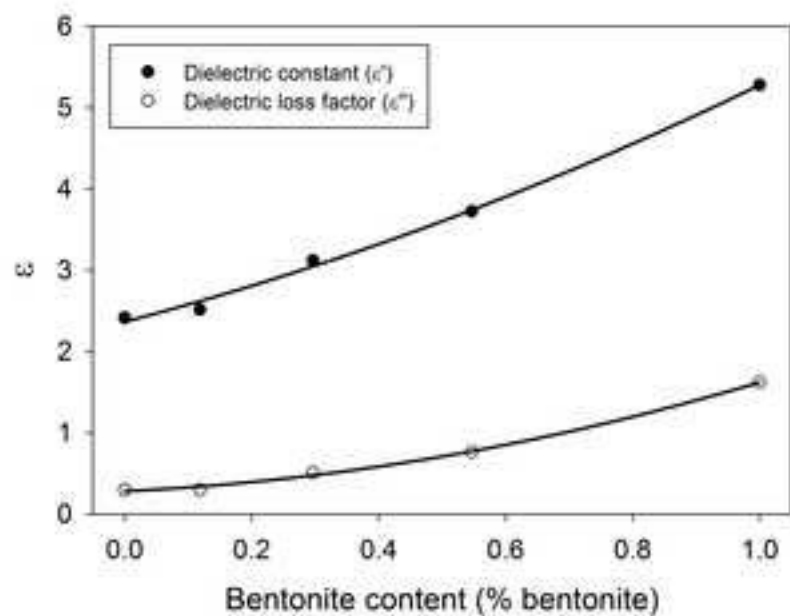
Figure 5



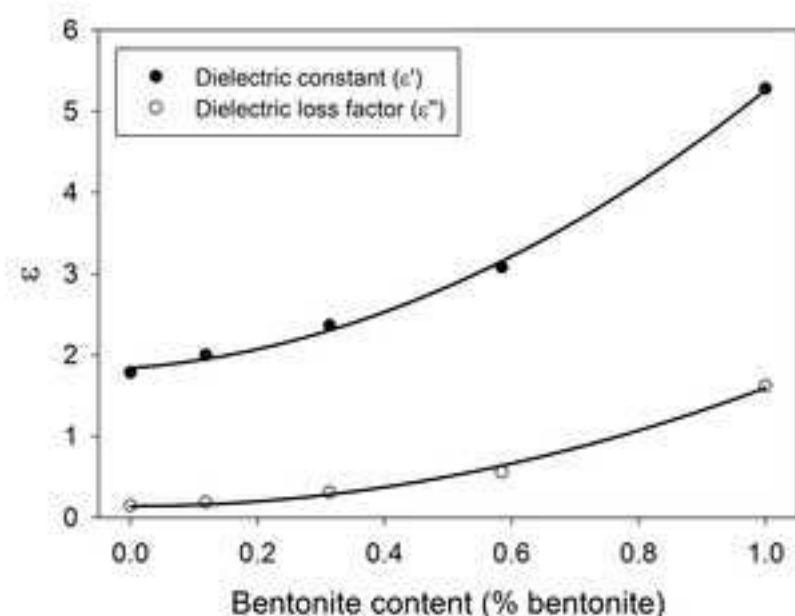
(a)



(b)



(c)



(d)