Microwave Materials Characterization of Geopolymer Precursor Powders

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***Abstract*— Geopolymers are structural materials that can be used as a viable alternative to ordinary portland cement concrete. However, their widespread adoption has been limited by the lack of understanding in their fundamental reaction mechanisms. Microwave characterization methods have shown promise at understanding these reaction mechanisms. However, the complex dielectric properties of geopolymer precursor powders and the effect of void content must first be understood. Therefore, in this work, the dielectric properties of two geopolymer precursor powders (blast furnace slag and fly ash) are measured. Then, the effect of void content and particle size distribution (PSD) is considered on the measured dielectric properties. By characterizing the inherent void content of these powder materials, this effect can be removed and therefore the true dielectric properties of the materials can be determined. The results show that the void content has a significant effect on the measured dielectric properties.**

Keywords*— *dielectric properties; geopolymer; microwave materials characterization; void content; loaded waveguide technique; fly ash; blast furnace slag

I. INTRODUCTION

Geopolymers are structural materials that can be used as a viable alternative to ordinary portland cement concrete [1]. Geopolymers are produced by reacting aluminosilicate and calcium powders with an alkaline solution to form a solid. Geopolymers have shown tremendous potential as a primary structural material in residential, commercial, and industrial applications. However, their widespread adoption is limited by the lack of understanding in their fundamental reaction mechanisms [2]. One important aspect of this reaction is the role of water. More specifically, during the reaction, the binding state of water has considerable influence on the mechanical and durability performance of these materials. To this end, microwave materials characterization methods are a promising approach to study this fundamental reaction [3], as they are sensitive to the presence of moisture and binding state of water [4]. However, a key requirement for microwave material characterization methods is the *a-priori* knowledge of the microwave (or dielectric) properties of the constituent powder materials used to make geopolymers (i.e., fly ash and blast furnace slag).

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The interaction of electromagnetic waves with dielectric (i.e., nonconductive) materials is described by the material's complex dielectric properties, $\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$ (when referenced to free space). The real part, permittivity, represents the ability of the material to store electromagnetic energy, and the loss factor (imaginary part) represents the material's ability to absorb electromagnetic energy. In the case of composite materials (such as concrete, geopolymers, or any mixture of dielectrics), the effective (overall) dielectric properties are related to the individual constituent dielectric properties and their respective volume fractions. These effective properties can be determined through the use of dielectric mixing models if the constituent dielectric properties and relative volume fractions are known [5].

Dielectric mixing models for homogenous media are dependent on the geometry of the inclusions, ratio (contrast) of the dielectric properties of the inclusion(s) and host media, etc. [5]. In the case of powder materials such as fly ash and slag, known as geopolymer precursor powders (GPPs), they are comprised of two materials; the GPP particles, and air that fills the inherent void content of the powder material. Once these GPPs are used to create a geopolymer, other materials will fill most of the void content (water, activating solution, etc.). In these cases, air can be considered as the homogenous host since the air fills all space where GPP particles are not present (i.e., akin to the dielectric host background). For spherical inclusions in a homogenous media (a reasonable assumption for powder-based materials characterized at microwave frequencies), the Silberstein mixing formula can be used to determine the effective dielectric properties of the mixture [5]:

$$\varepsilon_{eff} = \varepsilon_{powder}(1 - VF_{void}) + \varepsilon_{void} VF_{void} \qquad (1)$$

where VF_{void} is the volume fraction of the void content (air) and ε_{eff}, ε_{powder}, and ε_{void} are the complex dielectric properties of the mixture, powder, and void, respectively. In the case of this work, this mixing model will be used to determine the dielectric properties of the GPP from the measured effective dielectric properties. To this end, (1) can be rewritten to determine this quantity as:

$$\varepsilon_{powder} = \frac{\varepsilon_{eff} - \varepsilon_{void} VF_{void}}{(1 - VF_{void})}. \quad (2)$$

Therefore, if the effective dielectric properties and void content of the powder mixture are known (measured), the true dielectric properties of the powder particulate (GPP) can be determined.

The dielectric properties of a material are intrinsic and therefore independent of the measurement technique. There are a number of established dielectric property characterization techniques that can be employed including the free space method, cavity perturbation method, etc. [6]. However, these techniques come with limitations including a requirement for precise sample dimensions or limited applicability (for example, only low-loss materials). In addition, since these GPPs are in powder form, the use of some of the techniques to determine their dielectric properties is very difficult, if not impossible, as the material cannot be easily and specifically placed for measurement without a sample holder. As such, the filled waveguide technique is often a better choice for characterization of powder (or liquid) materials [7]. The filled waveguide method involves placing a material with unknown dielectric properties inside a section of waveguide and measuring its transmission and reflection properties with a Vector Network Analyzer (VNA). From these properties, the complex dielectric properties can be determined. This method is relatively easy to use, and has been shown to produce stable and accurate solutions for many solid materials [8]. However, powders are not rigid solids and therefore require additional measurement considerations. As such, the filled waveguide technique has been modified for powders and liquids [7]. In other words, this adaptation to the technique utilizes the placement of known dielectric slabs (or plugs) on either side of the material to contain the powder, thus ensuring the powder remains in the sample holder (waveguide) during measurement. This measurement configuration is illustrated in Fig. 1, and is shown in more detail in [7].

Dielectric measurements of powder materials also come with additional measurement challenges related to preparation of the sample to be measured. Specifically, the void content (i.e., volume fraction of air) within the powder sample will vary depending on how well the material is packed in the sample holder.

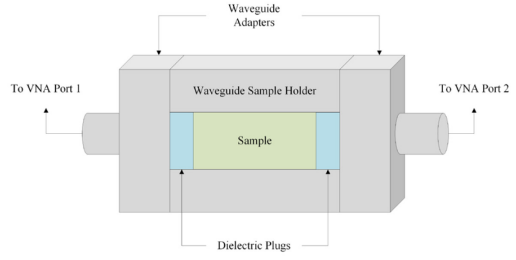

Fig. 1. Loaded waveguide measurement setup.

Thus, the measured dielectric properties, which are (as mentioned above) an effective value that depends on the powder material and air, will also vary with sample preparation. Thus, it is important to ensure that proper sample preparation has taken place. In other words, the sample must be prepared such that the void content is minimized and the sample compaction is maximized. Moreover, in order to determine the dielectric properties of the powder material itself (without the effect of void content) through proper application of dielectric mixing models, the void content must also be known.

II. MEASUREMENTS

As mentioned, a key requirement for utilizing microwave materials characterization methods to study geopolymer reactions is the *a-priori* knowledge of the dielectric properties of the GPPs without the effect of void content. Therefore, to determine these properties, two distinct sets of measurements must be performed. First, the effective dielectric properties of the material must be determined, and second, the void content of the material must be measured.

Many different powder materials can be used as GPPs. For the purpose of this study, Class F fly ash and blast furnace slag, each with three different particle size distributions (PSDs), were chosen due to their prominence in geopolymer mix designs [1]. Three different PSDs were used to measure the influence of particle distribution, size, and packing on microwave measurements. The three PSDs were produced by grinding the coarsest particles (Large PSD) into medium-sized particles (Medium PSD) and finer particles (Small PSD). The PSDs were measured using dry dispersion laser diffraction with Sympatec MYTOS equipment. The median particle diameter for each sample is shown in Table I.

A. Dielectric Properties

Dielectric properties are a function of frequency [9], and as such, a frequency band must be chosen to characterize the GPPs. Limited research into the dielectric properties of GPPs has been done [10]–[13]. Related to this, microwave materials characterization of cement-based materials has shown that frequencies in the R-, S- and X-bands are especially useful [14]–[16]. As geopolymers share many similar properties to cement-based materials, these frequency ranges are also likely to be good candidates for geopolymer studies as well. Thus, for this work, frequencies in the X-band (8.2 - 12.4 GHz) were used. Using the measurement setup shown previously in Fig. 1, the transmission and reflection properties (S-parameters) of the GPP samples were measured using a calibrated HP 8510C VNA. Since dielectric properties are independent of sample length, three different waveguide sample holders (lengths of 3.1 mm, 4.1 mm, and 5.1mm) were used. The complex (i.e., magnitude and phase) measured S-parameters (i.e., S_{11}, S_{21}, S_{12}, and S_{22}) are shown in Fig. 2 for blast furnace slag powder for different PSDs (measured using the 3.1 mm sample holder).

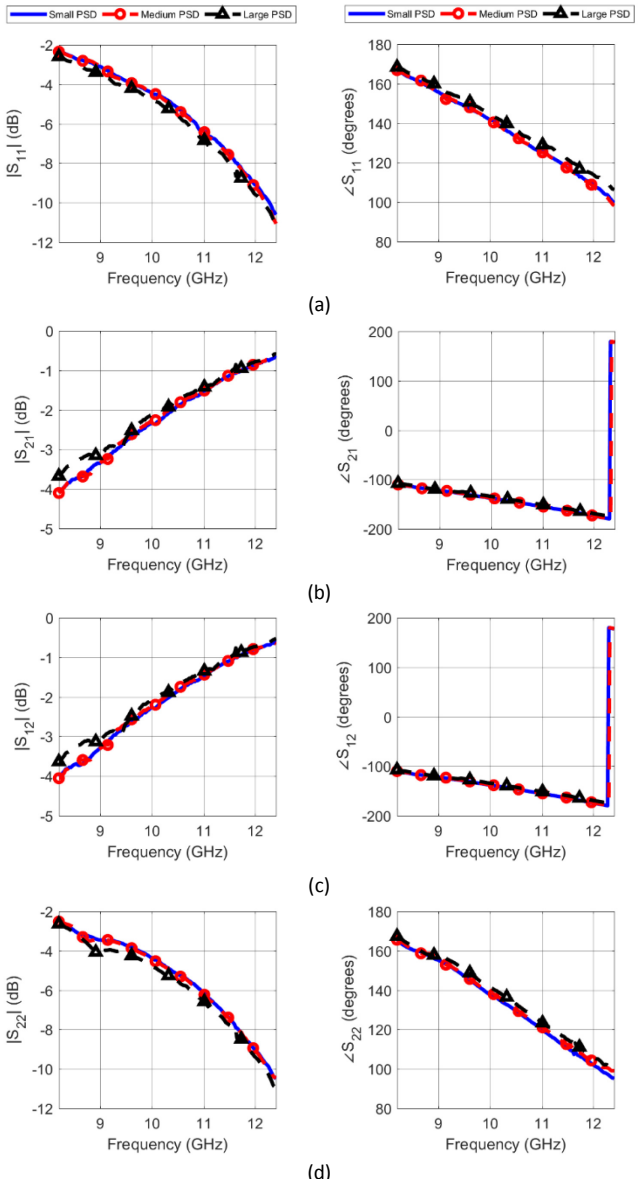

Fig. 2. Measured (a) S_{11}, (b) S_{21}, (c) S_{12}, and (d) S_{22} for blast furnace slag for different PSDs.

A few points can be made about the results of Fig. 2. First, the transmission and reflection response for all three PSDs show similar behavior as a function of frequency. Moreover, the magnitudes and phases of the small and medium PSD S-parameters are very similar, but the large PSD responses deviate slightly from those of the small and medium PSDs. This difference translates to a difference in the sample's effective dielectric properties. This change in dielectric properties may be due to a change in void content or in other material properties (i.e. particulate geometry/shape). In addition, measurement challenges such as geometric changes in the powder (i.e. large voids due to packing inconsistency) or discontinuities inside the waveguide (due to waveguide and/or plug alignment, etc.) can also cause measurement anomalies [17].

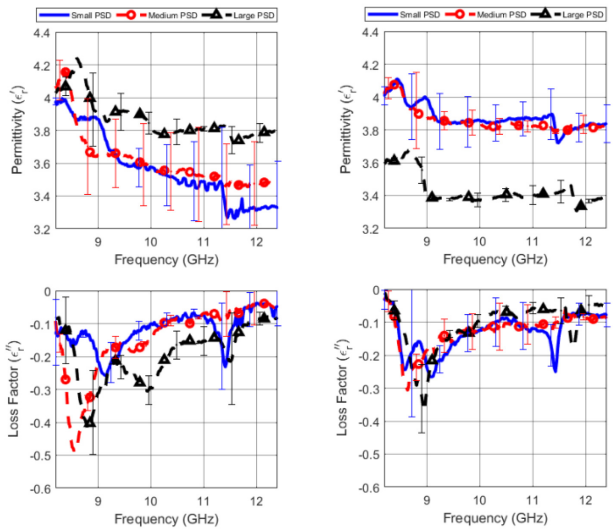

Fig. 3. Effective dielectric properties of fly ash (left column) and blast furnace slag (right column) for different PSDs.

Using the measured S-parameters, the dielectric properties of the material were subsequently calculated [7]. To calculate the dielectric properties, an initial guess must be supplied which may have a considerable effect on the result if not chosen properly. Thus, this initial guess value was chosen based on the assumption that the two precursor powders are low-permittivity and low-loss (i.e., similar to the properties of sand and mortar [18]). The average (of the 3 samples) and standard deviation of the calculated effective (including void content) permittivity and loss factor for the blast furnace slag and fly ash powders are shown in Fig. 3.

As shown, the calculated effective dielectric properties for fly ash and blast furnace slag are similar. It can also be seen that there are discontinuities in the dielectric properties around certain frequencies (mainly 8.75 and 11.5 GHz). As mentioned previously, geometric resonances (i.e., related to physical anomalies such as misalignment of the sample holder with the waveguide adapters, issues caused with the plug interfaces, etc.) can cause resonances in the measured S-parameters which subsequently cause discontinuities in the calculated dielectric properties such as those of Fig. 3. Therefore, although dielectric properties are a function of frequency, for dielectrics with low permittivity and loss in the microwave region, they should remain constant over a small frequency band (e.g., X-Band) [19]. To this end, the mid-band region (9.5 to 11 GHz) is considered for analysis. The average effective permittivity for small and medium PSDs of fly ash is 3.5, while the large PSD has an average effective permittivity of 3.8. For the average loss factor of fly ash, the small and medium PSD samples have a loss factor of –j0.1, and the large PSD has a loss factor of –j0.15. In addition, the standard deviation of the small and medium PSDs is much larger than that of the large PSD for permittivity. This may indicate measurement inconsistencies related to the different sample holders that cause resonant behaviors that are more prominent in the magnitude of the measured S-parameters (and hence the effect is more prominently noticed in the calculated permittivity).

The results for the blast furnace slag show a similar trend, with the effective permittivity for the small and medium PSD equal to 3.8, and the large PSD, a value of 3.4. For the loss factor, the small and medium PSD have a loss factor of –j0.12, and the large PSD, –j0.07. The same trend for standard deviation (of fly ash) is also evident for blast furnace slag.

The trends between the two sample types can also be considered. More specifically, for fly ash, the effective permittivity and loss factor of the large PSD is greater than that of the small and medium PSDs. However, for blast furnace slag, the effective permittivity and loss factor of the large PSD is less than that of the small and medium PSDs. This behavior may be attributed to the effect of void content. More specifically, as the void content in a sample decreases, the effective permittivity and loss factor will increase (and *vice-versa*). Thus, since the different PSD samples are comprised of the same constituents (GPP and air), the void content of the small and medium fly ash PSDs may be greater than that of the large PSD. Similarly, the void content of the large blast furnace slag PSD may be greater than that of the small and medium PSDs. These trends indicate a need for quantification of the particle shape itself, as this quantity effects the way the particles settle near one another and consequently also the overall void content.

B. Void Content

In addition to measuring the effective dielectric properties of the powders, the void content of each must also be known in order to determine the true dielectric properties of the GPPs. To this end, the void content of powder materials can be considered as similar to porosity of porous materials. Thus, traditional porosity measurement techniques can be used to determine the void content of GPPs. One reliable method of calculating porosity is by the method of gas expansion [20]. This involves placing the material (here, fly ash and blast furnace slag) in a chamber with a known volume ($V_{chamber}$) and filling the chamber with a small molecular volume gas (like nitrogen or helium) to a specified pressure (P_1). The added gas is then evacuated into a calibration chamber with known volume (V_{cal}) and the new pressure is measured (P_2). Then, the true (excluding air) volume (V_{true}) of the GPP can be calculated as:

$$V_{true} = V_{chamber} + \frac{V_{cal}}{1 - \frac{P_1}{P_2}}. \quad (3).$$

Then, the void content can be determined as the difference between the bulk volume (total physical volume of the sample), V_{bulk}, and the sample's true volume (or $V_{void} = V_{bulk} - V_{true}$). The material's bulk volume was determined by compacting the powder to completely fill a sample holder with known volume. Since the bulk volume of GPPs is a function of compaction, care must be taken during sample preparation to ensure measurement consistency. For this work, this was ensured by monitoring the mass of the samples. Specifically, the void volume of the fly ash and blast furnace slag was measured using a Quantachrome Ultrapyc 1200e pycnometer with nitrogen gas. To ensure that the effect of compaction is minimized, the void content measurement was repeated three times for each sample. Then, using the measured bulk and true volume, the void volume is calculated. From this, the void content (by volume, the parameter of interest for the mixing model) is the equal to the ratio of void volume to bulk volume $VF_{void} = V_{void}/V_{bulk}$. The resulting average measured void content and standard deviation is shown in Table I.

TABLE I. VOID CONTENT AND MEDIAN PARTICLE DIAMATER OF FLY ASH AND BLAST FURNACE SLAG FOR THREE PARTICLE SIZE DISTRIBUTIONS

Material	Void Content	Median Particle Diameter (μm)
Fly Ash - Small PSD	31.7% (+/- 0.90%)	22.9
Fly Ash - Medium PSD	31.9% (+/- 1.51%)	24.6
Fly Ash - Large PSD	27.2% (+/- 1.38%)	28.3
Blast Furnace Slag - Small PSD	48.9% (+/- 1.32%)	6.1
Blast Furnace Slag - Medium PSD	50.1% (+/- 1.24%)	6.4
Blast Furnace Slag - Large PSD	53.8% (+/- 1.69%)	7.5

As shown, the measured void content for fly ash and blast furnace slag follow the same trends as seen in the effective dielectric property measurements. That is, the void content of the large PSD samples is substantially different than small and medium PSD samples. For fly ash, the large PSD sample had over a 4.5% decrease in void content compared to that of the small and medium PSDs. For blast furnace slag, the large PSD sample had over a 4.5% and 3.5% increase in void content compared to that of the small and medium PSDs, respectively. Further, a comparison between the results of Fig. 3 and Table I shows that as the void content increases, the effective dielectric properties decrease and *vice-versa*. This is to be expected since a decrease in void content means an increase in the contribution of the particulate dielectric properties leading to an increase in the effective dielectric properties.

Now that the effective dielectric properties and void content have been determined, the Silberstein mixing formula (see (2)) can be used to calculate the true dielectric properties of the GPP, and are reported in Table II. The effective dielectric properties and void content for each material are also included.

TABLE II. EFFECTIVE DIELECTRIC PROPERTIES, VOID CONTENT, AND GPP DIELECTRIC PROPERTIES FOR FLY ASH AND BLAST FURNACE SLAG

Material	Effective Dielectric Properties	Void Content	True Dielectric Properties
Fly Ash Class F Small PSD	3.53 – j0.10	31.7%	4.71 – j0.15
Fly Ash Class F Medium PSD	3.57 – j0.12	31.9%	4.78 – j0.18
Fly Ash Class F Large PSD	3.80 – j0.16	27.2%	4.85– j0.22
Blast Furnace Slag Small PSD	3.85 – j0.12	48.9%	6.59 – j0.24
Blast Furnace Slag Medium PSD	3.83 – j0.12	50.1%	6.67 – j0.24
Blast Furnace Slag Large PSD	3.40 – j0.07	53.8%	6.19 – j0.16

The results show that void content has a significant effect on the effective dielectric properties for both permittivity and loss factor. This effect is more significant if there is a high void content in the GPP since the effective dielectric properties are less influenced by the powder's dielectric properties if there is (physically/volumetrically) less powder. The effect of void content is particularly interesting for the blast furnace slag and fly ash with large PSD. That is to say, the effective dielectric properties are considerably higher (fly ash) and lower (blast furnace slag) than for the other PSDs (see Fig. 3). However, after removing the effect of void content, the true GPP dielectric properties for the large PSD are still substantially different than the small and medium PSD for both fly ash and blast furnace slag. This difference may be attributed to the particulate geometry of the large PSD differing from those of the small and medium PSD and (again) indicates the need for further study into this aspect.

Overall, these results show that if the void content of powder GPPs is not considered, the measured effective dielectric properties may be significantly different than the true GPP dielectric properties. This difference may introduce considerable error when the effective dielectric properties are used as part of a more advanced analysis of geopolymer materials, since the effective dielectric properties contain the effect of void content that will likely be filled with another material (water or similar liquid filling the void content), as opposed to air as is the case here.

III. Conclusion

In this study, the effective dielectric properties and void content of two GPPs (with 3 different PSDs) were measured in order to study the effect of void content on dielectric property measurements. In addition, the void content was used, in conjunction with an appropriate dielectric mixing model, to determine the true dielectric properties of the GPP. The results indicate that the measured effective dielectric properties are significantly influenced by the void content in the GPPs. This effect is more significant if there is high void content in the GPP since the effective dielectric properties are influenced less by the powder's dielectric properties. Additionally, when powder GPPs are used as part of a geopolymer mix or undergo chemical reactions, the void content in the mix may be filled with other materials, thus changing the effective dielectric properties. This change in effective dielectric properties can have a significant effect on the accuracy of microwave materials characterization methods due to their reliance on accurate dielectric properties of the constituent materials. In addition, the void content measurement itself is also a function of sample (powder) compaction. This allows for additional error to be introduced if the compaction is not done properly. Thus, it may be beneficial to consider the specific gravity (density with respect to water) of the materials in question to determine void content in order to remove the dependence on compaction from the measurement approach entirely. Lastly, the effect of particle shape may also be considered as it relates to void content and subsequent dielectric property measurement.

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