Dielectric characterization of biodegradable wastes during pyrolysis

D. Beneroso¹, A. Albero-Ortiz², J. Monzó-Cabrera², A. Díaz-Morcillo², A.

Arenillas¹, J.A. Menéndez^{1*}

¹*Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*

²*Department of Communication and Information Technologies, Technical*

University of Cartagena, Cartagena, Spain

Corresponding author: Tel.: +34 985 119090

E-mail address: angelmd@incar.csic.es

Abstract

The lack of dielectric properties data has often been named as one of the reasons that has hampered the simulation of microwave processing of biomass feedstock and process design. In this work, the dielectric behavior of an organic fraction from municipal solid wastes during pyrolysis has been monitored as a function of temperature. Furthermore, the effect of the addition of a microwave absorbent material (carbonaceous char) to the raw biowaste upon the dielectric properties has been investigated for the first time.

The efficiency of the conversion of microwave energy to heat, measured by means of the $\tan \delta$ parameter, is shown in this study to be nearly 20 times higher when the absorbent char is added to the reaction bulk at room temperature and this gap is even greater in the 600 – 800 °C range. Nevertheless, the results suggest that the addition of increasing amounts of microwave absorbent (up to ca. 40%) impairs microwave penetration, which gives rise to a less homogeneous heating of the bulk. There is therefore an optimum proportion that balances heat conversion and penetration depth.

The results of this study lend support to the use of char as a means to induce thermochemical treatments by microwaves and reduce energy consumption in the process.

Keywords: Dielectric properties, Microwave pyrolysis, Biomass pyrolysis, Microwave heating modeling, Microwave absorbent

1. Introduction

On average, every one of the more than 500 million people living in the European Union (EU) throws away around half a ton of household rubbish a year. This is on top of the huge amount of waste generated from activities such as manufacturing (360 million tons) and construction (900 million tons), while the supply of water and the production of useful energy generate another 95 million tons. Altogether, the EU produces up to 3 billion tons of waste every year [1]. A significant proportion of waste going to landfill is organic material, (i.e. derived from both biomass and petroleum sources). Thermochemical conversion processes, involving pyrolysis and gasification, can convert this waste at source into potentially useful chemical feedstocks and fuels after the removal of the more readily recyclable materials, such as metals, glass, etc.

A number of processes are now under development or are at the demonstration stage, whose aim is to provide more cost-effective, environmentally and socially acceptable alternatives to incineration plants. One of these new technologies is microwave pyrolysis based on dielectric heating. This process benefits from the main advantages of using microwaves, such as rapid, volumetric and selective heating, and avoids the need to shred the feedstock and to pre-dry the samples, resulting in a substantial reduction in the costs associated with these steps [2-5]. In spite of these advantages, this technology has not yet reached industrial scale

owing to the lack of economic analyses on a large scale and the absence of sufficient data to quantify the dielectric properties of the input feedstocks.

The property that determines the dielectric response of material under the influence of an electric field is the relative complex permittivity, ϵ^* , which is expressed as a function of a real component known as the dielectric constant (which represents the ability of dielectrics to store electrical energy) and an imaginary component known as the dielectric loss factor (which represents the ability of a material to absorb the electric energy):

$$\epsilon^* = \epsilon' - j\epsilon''(1)$$

where $j = \sqrt{-1}$ and ϵ' and ϵ'' are the dielectric constant and the dielectric loss factor relative to the corresponding dielectric properties of free space.

An estimation of these properties is essential for the effective design and scaling up of microwave heating processes to ensure an accurate prediction of the absorbed power density; i.e. the rate at which the electromagnetic energy is converted to heat in the material. Dielectric properties may vary with composition, frequency, temperature and even material density [6] and, therefore, it is essential to characterize their variation in relation to those parameters.

Several studies have attempted to characterize the dielectric properties of coal [7] and some kinds of biomass [8, 9] since it is known that the dielectric loss of these materials at low temperatures is negligible, making them transparent to microwaves. However, when the substrates are subjected to higher temperatures (i.e. temperatures higher than 600 °C), the structures become essentially char, which is known to be a high microwave absorbing material due to the Maxwell-Wagner effect which causes a very high displacement of π -electrons on carbonized structures [10]. It is for this reason that different microwave receptor materials are added to biomass during microwave pyrolysis, so that a high enough temperature is reached to induce pyrolysis [11, 12]. However, most published studies are focused solely on the dependence of dielectric properties upon frequency radiation at room temperature [13-16] and ignore the need for a comprehensive study of the whole microwave pyrolysis process. In other words, an in-depth and extensive study of the dependence of dielectric properties on temperature is needed to obtain a better understanding of the dielectric response of organic substrates during microwave pyrolysis and of mixed organic substrates when used with microwave susceptors.

This paper investigates the microwave absorption capability of a biodegradable waste and its mixture with microwave absorbent char on the basis of their dielectric properties, from room temperature up to 800 °C at the commonly used frequency of 2.45 GHz.

2. Materials and Methods

2.1 Biowaste preparation and characterization

The biodegradable waste used for this study was an organic fraction from a municipal solid waste, obtained from a landfill in Seville (Spain). The waste was dried, partially cleaned of inerts such as glass or metals and size-reduced to 1-3 mm. This fraction has been labelled as MSWd. The pretreatment of this organic residue allows a good homogeneity of this fraction. Actually, this fraction has been used in other studies to produce synthesis gas by means of microwave-induced pyrolysis and the composition of the gas was quite homogeneous when repeating the tests [17].

In order to assess the effect of adding char as microwave absorber to the biowaste upon the dielectric response, a carbonaceous solid char was prepared by subjecting the biowaste sample to a temperature of 800 °C in an electric furnace for 1 h in an oxygen-free atmosphere. This has been labelled Char-MSWd. The mixtures of char:biowaste were prepared in weight ratios of 0.3:1 and 0.6:1. These two mixture ratios were considered on the basis of keeping the amount of char as low as possible to induce the microwave pyrolysis. In previous studies [17], we used 0.3:1 ratio; thus, we have used this same ratio in this work. Furthermore, a larger amount (0.6:1 ratio) was considered to study the effect of adding char to feedstock as microwave absorbent.

The moisture, ash content and volatile matter data of the residues were obtained on a LECO TGA-601 device. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The micro-analyzer provided data on the carbon, hydrogen, nitrogen, and

sulfur percentage composition. The oxygen content was determined using the LECO-TF-900 furnace. The results of proximate and ultimate analyses of the MSWd and char-derived samples are presented in Table 1.

Table 1. Proximate and ultimate analyses of the MSWd and Char-MSWd fractions

Residue		Municipal solid waste	Char from municipal solid waste
Label		MSWd	Char-MSWd
Proximate analysis (wt.%)	Moisture	2.8	3.3
	Ash ^a	27.7	66.6
	Volatile matter ^a	61.1	1.7
Ultimate analysis (wt.%)	C	45.1	30.7
	H	5.4	0.1
	N	2.1	1.0
	S	0.4	0.7
	O	19.3	0.9

2.2 Measurement of dielectric properties

An inverse methodology to obtain the permittivity of the different biowastes was used (Fig. 1) [18]. This technique is one of the most appropriate; other techniques such as standard coaxial probes may lead to lower precision since air bubbles below the coaxial probe can result in lower values of permittivity; resonant-cavity technique is typically used for low-loss materials (which is not our case) and identifying the resonant frequency and quality factor (intrinsic parameters of this technique) would have been difficult due to the high absorption of the materials. First, each sample (see Sample R in Fig. 1) was introduced and uniformly compacted into a quartz tube (i.d. 5 mm, height 43 mm; MSWd bulk density: 166 kg/m³; char bulk

density: 353 kg/m^3) and heated up to a specific temperature in an oxygen-free atmosphere by a GALLUR convection oven. The samples were subjected to 25, 50, 100, 200, 300, 400, 500, 600, 700, 800 and 1000°C before being very quickly placed (maximum 3 s) in the middle of a WR-340 waveguide where the scattering parameters (i.e., S_{11} , S_{12} , S_{21} and S_{22}) were measured by means of a RHODE & SCHWARZ, model ZVA67 vector network analyzer set to a frequency of 2.45 GHz. S-parameters describe the response of an N-port network to voltage signals at each port. The first number in the subscript refers to the responding port, while the second number refers to the incident port. Thus S_{21} means the response at port 2 due to a signal at port 1. Afterwards, the measurement system was modeled (Sample S in Fig. 1) by using CST Microwave Studio (CST MWS) commercial software and, by inverse techniques, the value of the complex permittivity of each sample at the corresponding temperature was obtained. That is to say, an optimization method (a genetic algorithm combined with a gradient descent optimization method) [18] was applied to the model to obtain a simulated material that would induce the same scattering parameters as those previously measured. As initial values for the corresponding optimization method, the permittivity of the materials was measured in a portable DIMAS dielectrometer, model DIELKITV/DIELKITC at room temperature. The errors during measurements are included in the Supplementary Material. Furthermore, to minimize the uncertainty of the sample cooling on the permittivity measurements during the sample transfer from the oven to the waveguide, the cooling curve was previously estimated and can be found in

the Supplementary Material. This curve allows establishing the operating temperature of the oven in order to reach the nominal temperature into the waveguide.

FIGURE 1

2.3 Loss tangent calculation

The loss tangent is an important dielectric property which is directly related to the ability of a specific material to convert electromagnetic energy into heat at a given temperature and frequency. This property is defined as:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2)$$

Furthermore, the relationship between the dielectric properties of biowaste and char was investigated for the two material mixtures over the selected temperature range. The dielectric properties of a mixture of two different materials can be modeled by using different equations such as the Landau, Lifshitz and Looyenga equation (Equation 3), as reported in [19]:

$$\epsilon^{* \frac{1}{3}} = v_{MSWd} \left[\epsilon_{MSWd}^{* \frac{1}{3}} - \epsilon_{char-MSWd}^{* \frac{1}{3}} \right] + \epsilon_{char-MSWd}^{* \frac{1}{3}} \quad (3)$$

where v_{MSWd} is the volumetric fraction of the material MSWd, which was calculated from its density, and ϵ_{MSWd}^* and $\epsilon_{char-MSWd}^*$ are the permittivity of the biomass and char fractions, respectively. The accuracy of this model was

tested using the experimental data obtained over the temperature range selected.

2.4 Skin depth calculation

The skin depth, also known as penetration depth (D_s), is defined as the distance from the surface into the materials at which the travelling electromagnetic wave power drops to e^{-1} from its value at the surface. The skin depth can be calculated using Equation 4 [20]:

$$D_s = \frac{\lambda_0 \sqrt{\epsilon''}}{2\pi \epsilon''} \quad (4)$$

where λ_0 is the microwave wavelength in free space. The skin depth is an important parameter since the use of microwaves as a heating medium usually involves scaling-up limitations due to the difficulty of properly dispersing the microwaves as the material increases in volume [21].

3. Results and Discussion

The measured dielectric properties of the MSWd and Char-MSWd fractions are shown in Fig. 2 (a) and (b), respectively, versus the increase in temperature. As can be seen, the dielectric properties depend greatly on the temperature during pyrolysis, particularly at high temperatures.

FIGURE 2

The dielectric constant and loss factor for MSWd show a nearly constant value from room temperature up to 500 °C, corresponding to the pyrolysis

step. A sharp increase in the dielectric constant is observed beyond 600 °C corresponding to development of char formation that shows a maximum value at 800 °C. In the case of the loss factor, there is a gradual increase up to 800 °C as a consequence of the higher conductivity of the sample because of the occurrence of π -electron conduction when aromatized structures are formed during pyrolysis [7, 10]. Although not graphed in this paper, a further temperature increase up to 1000 °C exponentially increased the loss factor up to $\epsilon'' \approx 13$.

The Char-MSWd fraction follows the same dielectric constant pattern as the MSWd fraction, although it reaches much higher values. Of particular interest is the very high value even at room temperature, due to the greater capability of the carbon to store electrical energy from microwaves. However, the evolution of the loss factor with increasing temperature is quite different from that of MSWd. As can be seen in Fig. 2(b), the loss factor is $\epsilon'' = 12$ at 800 °C; this value is similar to that of the MSWd fraction at 1000 °C, as reported above, which suggests that the higher the char concentration is, the lower the temperature required to reach large loss factors. Thus, it seems that the initial characteristics of the starting material have a significant influence on dielectric behavior during pyrolysis despite the fact that the solid material produced must be the same at the end of pyrolysis (char).

In addition, the loss factor peaks indicate a typical relaxation polarization behavior [7]. During the measurement of the dielectric properties of the

Char-MSWd fraction, different local power absorption rates along the sample volume in the form of thermal runaway effect could have taken place and, therefore, increased the measurement uncertainty and loss factor fluctuation. This is not the case of the MSWd fraction, whose loss factor does not show any fluctuation.

Fig. 3 shows the variation of the $\tan \delta$ parameter for the MSWd and Char-MSWd fractions.

FIGURE 3

At lower temperatures (<500 °C), the thermochemical decomposition of organic matter takes place, and the polar compounds that might have contributed to the heating of the material are quickly released. Thus poor $\tan \delta$ values (≈ 0.02) are attained in the case of the MSWd fraction. In the 500 - 600 °C range, $\tan \delta$ increases up to 0.35, but it decreases again after 600 °C. From an energetic point of view, the 500 – 600 °C range seems to be the most suitable for minimizing the consumption of energy during pyrolysis. However, a radical increase in $\tan \delta$ (≈ 7.5) was observed at 1000 °C (not shown in Fig. 3). In the case of the Char-MSWd fraction, $\tan \delta$ is higher at low temperatures (≈ 0.40), which means that under these conditions char is a microwave absorbent material and so it can be used to induce the pyrolysis of biowastes and other biomass feedstock. This value is similar to those previously reported for similar materials, such as carbon black (0.35-0.85) and charcoal (0.11-0.29) at room temperature and 2.45 GHz [10]. However, it can be seen that at temperatures higher than 600 °C,

the microwave absorption capability decreases and $\tan \delta$ approaches that of water ($\tan \delta = 0.118$ at 2.45 GHz and 25 °C). A similar behavior was observed in the case of the char from oil palm shell [22]. This tendency has not yet been explained, but it is probably related to the fact that the dielectric constant increases monotonically with temperature, while the loss factor remains essentially within the same narrow range ($\epsilon'' \approx 5-12$).

The dielectric behavior of mixed biowaste and char was also investigated, for which an intermediate response somewhere between that obtained for the MSWd and char fraction was initially expected. The dielectric properties for the 0.3:1 and 0.6:1 mixtures obtained using the Landau, Lifshitz and Looyenga model are shown in Fig. 4 and Fig. 5 respectively, along with the experimental measurements. The values for temperatures lower than 500 °C are also included at a higher scale to make them clearer. The model predicts the tendency of the measured dielectric constant values slightly well. Nevertheless, the loss factor is not modeled accurately, especially in the 600 – 800 °C range, as it underestimates the experimental values. This suggests the occurrence of a thermal runaway effect when the organic feedstock is mixed with a microwave absorbent material, leading to the boosting of heat loss at lower temperatures compared to pure biowaste pyrolysis. This phenomenon occurs because the microwave energy is concentrated in the microwave absorbent (usually metallic oxides and carbonaceous materials), whose rate of absorption (referred to as thermal absorptivity) increases with temperature, leading to an exponential increase in the heating rate [23].

Consequently, microwave power needs to be properly controlled, especially beyond 600 °C, to avoid a dramatic increase in temperature.

FIGURE 4

FIGURE 5

In addition, the effect of the concentration of the microwave absorbent on $\tan \delta$ is shown in Fig. 6. At lower temperatures, $\tan \delta$ seems to remain approximately the same regardless of the char concentration. However, in the 200 - 700 °C range, the higher char concentration (0.6:1 mixture) provides a better conversion of microwaves into heat, especially in the 500 – 700 °C range. As shown in Fig. 5, thermal runaway starts at a lower temperature in the case of a higher char concentration. Nevertheless, it is the lower char concentration that provides a more efficient heating at 800 °C. Again, this suggests that it is the initial characteristics of the starting material (in this case, the different char concentration) that determine dielectric behavior despite the fact that the final product is char.

From the observations made so far it follows that dependence of the dielectric properties on temperature must be taken into account when designing a microwave applicator to ensure an energy efficient operation and so obtain the desired products. For instance, the production of syngas (H_2+CO) from biowaste is highly favoured at 600 – 800 °C during microwave-induced pyrolysis, which matches with the highest energy conversion to heat [17]. As a means of comparison, the evolution of the loss tangent in the case of MSWd has been included in Fig. 6.

FIGURE 6

1 It can be seen that the addition of the microwave absorbent char improves
2 the conversion of electromagnetic energy into heat, the loss tangent being
3 ca. 17 times higher at room temperature (0.33 vs 0.02). This is an
4 encouraging result for the scaling-up of microwave-induced pyrolysis,
5 because the addition of char to the feedstock to be pyrolysed will contribute
6 greatly to a reduction in energy requirements and costs. In a recent report, a
7 reduction of 30% in energy expenditure was reported by properly mixing the
8 organic feedstock with 10 wt.% char [24]. Consequently, the most
9 appropriate way to carry out microwave-induced pyrolysis at high
10 temperature is to use char as microwave absorbent mixed with the organic
11 feedstock.

12 Besides, as reported in the Introduction, microwave processing avoids the
13 need for pre-drying the feedstock. However, a pre-treated sample has been
14 used in this work. As a means of comparison, the effect of the moisture
15 content on the dielectric properties of the residue was measured (at 25 °C):
16 $\tan \delta$ parameter increased up to 0.6 compared to 0.3; moisture can then
17 slightly improve the microwave absorption of the residue at low
18 temperature.

19 The skin depth of these mixtures during pyrolysis is illustrated in Fig. 7. A
20 peak corresponding to the highest microwave skin depth was observed at
21 400 °C, as also reported by [25]. This is assigned to the onset of the
22 pyrolysis, when volatiles begin to be released. However, a remarkable
23 decrease in the skin depth is observed beyond 400 °C, which indicates
24 strong microwave absorption by the char because of the high density of π -

1 electrons. Throughout the pyrolysis process, the 0.6:1 mixture exhibits lower
2 skin depths due to the higher concentration of microwave absorbent char,
3 which is not surprising given its dielectric properties and hence higher
4 microwave absorption capability.

5 **FIGURE 7**

6 Two opposing effects then can be inferred from the microwave-absorbent
7 concentration used to maximize both the skin depth and microwave
8 absorption, as shown in Fig. 8. On the one hand, for homogeneously blended
9 mixtures, the skin depth is greater at low char concentrations (Fig. 7)
10 because a larger amount of transparent material (biowaste) is present,
11 which ensures a more homogeneous heating, although it is possible that
12 more energy will be consumed (Fig. 6). On the other hand, microwave
13 absorption is greater at high char concentrations where the penetration
14 depth is smaller since char is produced preferentially on the outer surfaces,
15 leading to a more heterogeneous heating. These effects may have a direct
16 influence on the process performance. For instance, the effect of char
17 concentration on the microwave-induced pyrolysis of the biowaste used in
18 our study to produce syngas was found to be determinant [12]. In their
19 study, Beneroso *et al.* found that a low char concentration led to a higher
20 syngas concentration in the gas from the pyrolysis, probably due to the
21 greater penetration depth of microwaves into the bulk which led to a more
22 homogenous heating.

23 **FIGURE 8**

4. Conclusion

The dielectric properties of an organic fraction from a municipal solid waste were determined at 2.45 GHz from room temperature to 800 °C. The dielectric properties of the biowaste remained constant during pyrolysis up to 400 °C; then there was a sharp increase in both the dielectric constant and loss factor, owing to the release of volatiles and honeycomb-like carbon structures with a high delocalised electron density. Furthermore, the addition of char as microwave absorbent to the feedstock proved to be an effective way to reduce the energy consumption of the pyrolysis process, because it provided the bulk with a high $\tan \delta$ at room temperature, although it reduced the penetration depth, which resulted in a more heterogeneous heating when a high concentration of char was used.

The dielectric characterization addressed in this paper could serve as a starting point for the design of suitable equipment to perform the microwave-induced pyrolysis at industrial scale with the appropriate simulation software.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement n° 311815 (SYNPOL project). D. B. also acknowledges the financial support received from PCTI and FICYT of the Government of the Principado de Asturias.

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Figure captions

Figure 1. Inverse methodology for determining the dielectric properties based on the procedure described in [18]

1

2 **Figure 2.** Dielectric properties of the (a) MSWd fraction (b) Char-MSWd
3 fraction during pyrolysis.

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2 **Figure 3.** Evolution of $\tan \delta$ during pyrolysis for the (a) MSWd and (b)
3 Char-MSWd fractions.

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2 **Figure 4.** Dielectric constant of the mixtures

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2 **Figure 5. Loss factor of the mixtures**

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2 **Figure 6.** Evolution of $\tan \delta$ during pyrolysis for the different char/biowaste
3 mixtures. $\tan \delta$ from MSWd fraction is also depicted as a means of
4 comparison

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1

2 **Figure 7.** Microwave skin depth for the mixtures of MSWd with Char-
3 MSWd during pyrolysis

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Figure 8. Effect of the microwave absorbent (mw absorbent) concentration on the microwave heating efficiency. In the initial phase, only the added microwave receptor is able to absorb microwaves and produce heat, which allows the nearby particles of the mw transparent biowaste to be heated by convection, conduction and radiation. Later, the removal of volatiles produces char, which will act as a mw absorbent, enabling the pyrolysis process to be sustained. Depending on the concentration of the initial mw absorbent, first, secondary, tertiary, etc. generations of mw absorbents may be obtained. Unlike the case of high char concentration, better penetration depths are attained at low char concentrations, making it possible to develop larger generations of mw absorbents during pyrolysis, and thereby facilitating more homogeneous heating

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Supplementary material

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Error in measurements

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MSWd sample

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Mixture Char:MSWd (0.3:1)

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Mixture Char:MSWd (0.6:1)

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Char sample

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Cooling down curve

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