

Relationships between dielectric properties and characteristics of impregnated and activated samples of potassium carbonateand sodium hydroxide-modified palm kernel shell for microwave-assisted activation

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Abstract

The aim of this work was to evaluate the dielectric properties of impregnated and activated palm kernel shells (PKSs) samples using two activating agents, potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH), at three impregnation ratios. The materials were characterized by moisture content, carbon content, ash content, thermal profile and functional groups. The dielectric properties were examined using an open-ended coaxial probe method at various microwave frequencies (1–6 GHz) and temperatures (25, 35, and 45°C). The results show that the dielectric properties varied with frequency, temperature, moisture content, carbon content and mass ratio of the ionic solids. PKSK1.75 (PKS impregnated with K_2CO_3 at a mass ratio of 1.75) and PKSN1.5 (PKS impregnated with NaOH at a mass ratio of 1.5) exhibited a high loss tangent (tan δ) indicating the effectiveness of these materials to be heated by microwaves. K_2CO_3 and NaOH can act as a microwave absorber to enhance the efficiency of microwave heating for low loss PKSs. Materials with a high moisture content exhibit a high loss tangent but low penetration depth. The interplay of multiple operating frequencies is suggested to promote better microwave heating by considering the changes in the materials characteristics.

Key words: activation, dielectric properties, impregnation, palm kernel shell, penetration depth

1. Introduction

Microwave heating has been recognized as a promising alternative to conventional heating and a green processing approach in various physical and chemical processes such as catalytic heterogeneous reactions, disposal of hazardous wastes and pyrolysis of various organic wastes [1]. Microwave is also used to promote heating of agro-wastes such as palm kernel shells, rice husks, oil palm fibers and switchgrass for the synthesis of biochar and biofuel [2,3]. In addition, a microwave-assisted activation of a carbonaceous biomass that yields activated carbon with high surface area similar to that obtained from conventional heating can be achieved with a suitable activating agent [4].

The efficacy of microwave heating is directly associated with the dielectric properties of the materials. The dielectric properties define the interaction between the electromagnetic field and the material which is crucial to ensure that the material can be heated under microwaves with uniform heating and a good end-product quality with a satisfactory penetration depth of the microwave energy [5,6]. Yet, the underlying principles of dielectric properties are often neglected in many of the microwave-assisted processes even though they are im-

perative in microwave heating mechanisms [7].

The dielectric properties (or permittivity, ε^*) are expressed as follows:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

, where ε ' is the dielectric constant (real part of permittivity), that is, a measure of how much energy from an external electric field is stored within a material through the polarization mechanism, while ε '' is the loss factor (imaginary part of permittivity) which represents the ability of a material to absorb and dissipate the electromagnetic energy into heat. The loss tangent ($\tan \delta$) is used to describe how efficient the electromagnetic energy stored within a material is converted into heat at a specific frequency and temperature. It is given as

$$\tan \delta = \varepsilon^{"}/\varepsilon'. \tag{2}$$

The dielectric properties can assist in examining microwave heating and material interactions, predicting the heating rates, and describing the heating characteristics and behavior of a material when it is subjected to a high-frequency electromagnetic field [8]. Penetration depth, $D_{\rm P}$, is used to determine how far the electromagnetic power can go inside a material, and it is given as follows:

$$D_{P} = \frac{\lambda_{o} \sqrt{\varepsilon'}}{2\pi \varepsilon''} \tag{3}$$

, where λ_o is the free space microwave wavelength (for 2.45 GHz, λ_o =12.2 cm). The volumetric heating of microwaves could be less operative for a material with a short penetration depth when only a small portion of material thickness absorbs the microwaves. Consequently, the heating would not be uniform due to the poor strength of the electromagnetic wave at the material core that farther the penetration depth [7,8].

There are not many studies on the dielectric properties of materials in relation to microwave-assisted activation of activated carbon in the literature. Salema et al. [2] reported an increase in carbon content that enhances the dielectric constant (ε') of char compared to that of an oil palm biomass. The dielectric properties of impregnated biomass samples such as K₂CO₃-impregnated cempedak peel [9], NaOH-impregnated cempedak peel [10], KOH-impregnated palm kernel shell [11], and ZnCl₂-impregnated palm kernel shell [12] at different concentrations showed the promising role of activating agents as a microwave absorber in chemical activation. However, the relationships between the dielectric properties and the characteristics of a raw material, impregnated sample and activated carbon representing the complete chain of microwave-assisted activation is still limited and hence should be established. Therefore, the objective of the present work was to evaluate the dielectric properties of a commonly used activated carbon precursor, namely palm kernel shells, in relation to the characteristics of the modified samples. Two activating agents, potassium carbonate (K2CO3) and sodium hydroxide (NaOH), were used for various assays of impregnated and activated samples. In this work, we evaluated the dielectric properties of samples at the impregnation stage and activation stage, respectively. The changes and relationships between the characteristics and dielectric properties of the materials were discussed to shed some light on factors that can provide positive effects in microwave-assisted activation.

2. Experimental

Palm kernel shells (PKSs) were obtained from a palm oil factory in the Johor State of Malaysia. Analytical-grade sodium hydroxide (NaOH), potassium carbonate (K₂CO₃) and hydrochloric acid (HCl) were obtained from a local manufacturer.

The precursor was washed with distilled water and dried in oven at 110°C for 24 h. Then, it was ground and sieved to a size of 500 μm . Twenty grams of PKSs were mixed with different mass ratios (activating agent to precursor) of 1.0, 1.5 and 2.0 for NaOH and 0.75, 1.25 and 1.75 for $K_2\text{CO}_3$. The solid-electrolyte solution mixtures were stirred at 90°C for 50 min. After that, the mixtures were dried in oven at 110°C for 24 h for impregnation.

The impregnated samples were activated using furnace at 500°C for 2 h. The resultant activated carbons were washed with 0.9 M HCl and then rinsed thoroughly with distilled water to a constant pH. The pyrolysis of the PKSs under the same heating conditions yields a char. The samples were designated as PKS-C, PKSK and PKSN for char, potassium carbonate-impregnated and sodium hydroxide-impregnated samples, respectively. The term AC- that precedes PKSK and PKSN was designated to represent the samples that had undergone heating (activation) at 500°C for 2 h, while the numerals at the end of the sample name indicate the impregnation ratio. For example, AC-PKSK1.75 is a PKS impregnated with K₂CO₃ at a ratio of 1.75 followed by activation at 500°C for 2 h.

Moisture content is the percentage of free water in the sample and was calculated as $(w_i - w_d) \times 100/w_d$, where $w_i(g)$ is the initial mass of sample, and w_d (g) is the mass of the sample after drying in an oven at 110°C for 24 h. Ash content is the amount of leftover or minerals when the volatiles and organic matters are liberated from the sample at 800°C for 2 h and was calculated as $w_f \times 100/w_d$, where $w_f(g)$ is the mass of the ash. The carbon content of the PKS, char and activated carbons were estimated with EDX (X-MaxN 50 mm²; Oxford Instrument, UK). Fourier transform infrared spectroscopy combined with attenuated total reflectance (IRTracer-100; Shimadzu, Japan) was used to determine the surface functional groups. Thermogravimetric analysis (TGA) was performed to obtain the thermal decomposition profile of the PKS. The PKS was subjected to a N₂ flow at a heating rate of 10°C/min to 950°C using a TGA4000 (PerkinElmer, USA). The specific surface area of the adsorbents was determined with a Pulse ChemiSorb 2705 (Micrometrics, USA) at a liquid N₂ temperature of 77 K. The surface area was calculated with the single-point Brunauer-Emmett-Teller method

The dielectric properties of all the samples were measured at various microwave frequencies (1–6 GHz) and temperatures (25, 35, and 45°C) using an open-ended coaxial probe technique. The measurement system consists of a coaxial probe (HP 85070D) attached to a Vector Network Analyzer (VNA model HP 8720B). The measurement of each sample was repeated five times to ensure good reproducibility of the results [2].

3. Results and Discussion

3.1. Characteristics of samples

Fig. 1 shows the thermal degradation of PKSs. The peak at a temperature below 100°C indicates the loss of moisture, while the peaks at 250 and 350°C are due to the oxidation of functional groups and the removal of volatile matters [13]. From Fig. 1, the temperature between 400 and 500°C could be adequate to activate the PKSs because of the stable derivative weight loss (about 75% weight loss). However, the types of activating agents and the impregnation ratios may also affect the development of a porous structure and the surface area of palm kernel shell-based activated carbon at the selected carbonization (activation) tem-

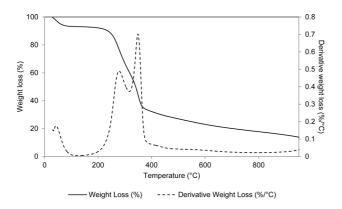


Fig. 1. Thermal degradation of palm kernel shells.

perature.

Table 1 shows the characteristics of impregnated and activated samples derived from palm kernel shells (PKSs) using K₂CO₃ and NaOH. The NaOH-impregnated samples (PKSN series) had a higher moisture content compared to the K₂CO₃impregnated samples (PKSK series). On the other hand, the AC-PKSN series had a greater moisture content followed by the AC-PKSK series and PKS-C. Generally, the moisture content of activated carbons increased with the increasing impregnation ratio of K₂CO₃ and NaOH. This could be partly due to the hygroscopic nature of the leftover activating agents (in the form of ash minerals) that have the ability to absorb moisture from their surroundings. The NaOH-activated carbons (AC-PKSN series) had a higher moisture content compared to the K₂CO₃-activated carbons (AC-PKSK series) due to the greater specific surface area of the former. As the pore volume increases, more water vapor can readily and physically be adsorbed onto the textures of the activated carbon.

The NaOH-activated carbons had a higher ash content compared to the $\rm K_2CO_3$ -activated carbons, PKS and PKS-C. The ash content increases as the ratio of NaOH increases. The increase of the ash content could be attributed to the intercalation of unreacted inorganic sodium compounds with a high boiling temperature (1388°C) in the material matrix upon activation. The carbon content of the $\rm K_2CO_3$ -activated carbons is similar with a small difference of 0.2–1.0%, while that of the NaOH-activated carbons decreased with an increasing NaOH ratio. A high ash content in the AC-PKSN series could be the reason for the low specific surface area of the activated carbons when compared with the commercial ones [14]. On the other hand, the conditions for $\rm K_2CO_3$ activation may not be suitable to activate PKSs

Table 1. Character	ristics of the palm kernel shell	l-modified samples			
Sample	Moisture content (%)	Ash content (%)	Carbon content (%) ^{a)}	Yield (%)	Surface area (m ² g ⁻¹) ^{b)}
PKS	5.64	19.6	60.5	-	-
PKS-C	0.36	15.3	84.3	26.0	69.4
PKSK0.75	4.18	-	-	-	-
PKSK1.25	15.8	-	-	-	-
PKSK1.75	12.2	-	-	-	-
PKSN1.0	37.2	-	-	-	-
PKSN1.5	40.6	-	-	-	-
PKSN2.0	23.8	-	-	-	-
AC-PKSK0.75	2.92	12.1	88.2	18.5	5.29
AC-PKSK1.25	3.6	8.41	88.5	21.1	53.0
AC-PKSK1.75	4.04	14.2	87.5	23.7	23.8
AC-PKSN1.0	6.07	33.8	62.2	43.6	145
AC-PKSN1.5	11.8	54.6	52.2	28.9	251
AC-PKSN2.0	17.0	73.4	31.8	20.1	458

^{a)}Surface carbon content by energy-dispersive X-ray spectroscopy.

b) Single-point Brunauer-Emmett-Teller surface area.

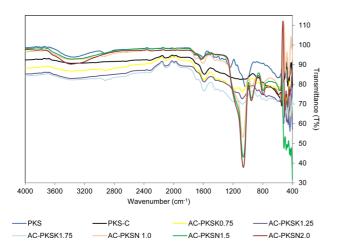


Fig. 2. Functional groups of the K₂CO₃- and NaOH-activated samples.

because of aggressive heating and excessive burning-off leading to a small yield and poor surface area development.

The yield of the AC-PKSN series decreased as the ratio of NaOH was increased. Additionally, the carbon content for this series decreased when the impregnation ratio was increased. It has been suggested that NaOH chaotically strips and decomposes the volatiles via oxidation for effective chemical activation, hence decreasing the carbon content. In addition, the boiling point of NaOH, which is higher than the activation temperature (500°C), could result in an increase of the ash content which may as well decrease the carbon content. Nevertheless, the surface area of the AC-PKSN series is proportional to the ratio of NaOH. In contrast, the surface area of the PKS-C is higher than that of the AC-PKSK series. The specific surface area of K₂CO₃-activated carbons signifi-

cantly decreased despite the increase of the carbon content. This could be a result of the excessive burning-off by the potassium salt which may in addition demolish the porous textures during activation.

The FTIR spectra of the PKS, char and activated samples are shown in Fig. 2. PKS contains carboxylic acids (O-H, 3310 cm⁻¹), alkanes (C-H, 2910 cm⁻¹), alkenes/aromatic rings (C=C, 1580 cm⁻¹), and esters/ethers (C-O, 1031 cm⁻¹; Ar-O, 1237 cm⁻¹). The wavenumber of 3600–3200 cm⁻¹ is normally attributed to the moisture content. After carbonization, PKS-C had missing peaks of C-O stretch (1031 cm⁻¹) and alkanes stretch (C-H, 2910 cm⁻¹). However, the alkynes (C≡C, 2081 cm⁻¹) appeared in the PKS-C and K₂CO₃-activated samples. All activated samples showed similar functional groups with varying intensities for different impregnation ratios. K₂CO₃ contributes to the presence of the alkanes stretch and amine groups in the activated samples. The assignments of the AC-PKSK series are alkanes stretch (C-H), alkynes (C=C, C-H), aromatic rings (C=C), alcohols, carboxylic acids (C=O, O-H) and amines (C-N). Similarly, the AC-PKSN series showed spectra with peaks attributed to carboxylic acid (O-H, C=O), amines (C-N), aromatics (C-H, C=C), alkynes (C=C) and alkanes (C-H). The peaks increased intensely as the NaOH ratio was increased, while C-X, C=C bending, C≡C and C–H groups diminished upon activation.

3.2. Frequency-dependency of the dielectric properties

Figs. 3 and 4 show the effect of frequency on the dielectric properties of the K_2CO_3 - and NaOH-modified samples (impregnated and activated) at room temperature. The frequency was divided into three regions, namely low (1–2.5 GHz), medium (2.5–4.5 GHz) and high (4.5–6 GHz).

Figs. 3(a, d) and 4(a, d) show the variations of the dielectric

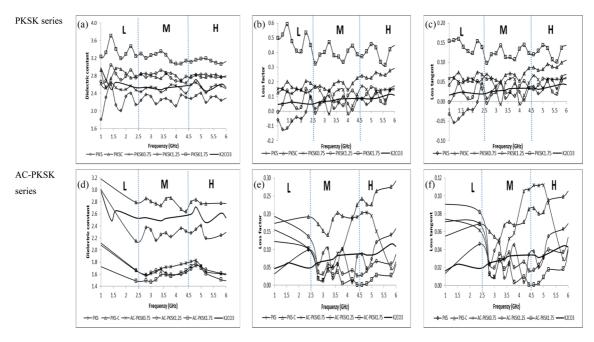


Fig. 3. Dielectric properties of the K_2CO_3 -modified samples at room temperature.

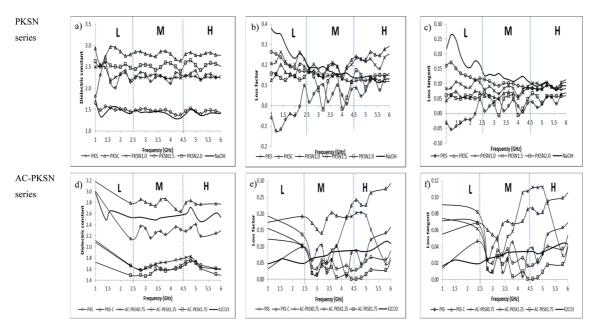


Fig. 4. Dielectric properties of the NaOH-modified samples at room temperature.

constant (ε ') of the K_2CO_3 - and NaOH-modified samples with the frequency. The pattern of ε ' at the low and high frequency regions could be explained by the Maxwell-Wagner polarization and/or ionic conduction within the material, in which a small movement of charges at high frequency may result in the alignment of charge dipoles [11]. At the low frequency region, the presence of moisture could be the main reason for the increase of ε ' despite the rapidly diminished conductive effect of microwave heating [2]. PKSK1.75 has the highest value of ε ' followed by PKSK1.25, PKSK0.75, PKS-C and PKS. This is in agreement with a reasonable amount of moisture in the samples, and the influence of the hygroscopic K_2CO_3 in the impregnated series which brings about the high value of ε '.

On the other hand, the ε ' of the NaOH-impregnated samples decreased as the frequency was increased as a result of the polarization effect due to the varying electric field [2]. For example, PKSN2.0 had a higher ε ' than that of PKSN1.0 and PKSN1.5. It is inferred that the amount of NaOH could modify the ε ' of the impregnated samples. In such circumstances, the moisture content may not necessarily be the determining factor that affects ε '. The ε ' of the NaOH-activated carbons decreased as the frequency was increased at the low frequency region. However, there is no clear trend at the middle and high frequency regions. The inconsistency of ε ' could be caused by the electric field distribution and the phase of the wave travelling through the material [15]. At the low frequency region, PKS-C and NaOH had the highest and the lowest ε ', respectively. Among the AC-PKSN series, AC-PKSN1.5 had the highest ε ' followed by AC-PK-SN1.0 and AC-PKSN2.0. This could be due to the high moisture content and the carbon content [7,10]

PKS-C has a higher ε ' than PKS and the AC-PKSK and AC-PKSN series. The ε ' of PKS is lower than that of PKS-C probably due to the high carbon content of PKS-C (84.3%) compared to that of PKS (60.5%). Other factors besides the moisture content such as the ash content, carbon content and functional

groups could also offer positive effects on ε ' [7,10]. Hence, ε ' is a complex function that varies especially when there is a change in the intrinsic properties of the material during activation.

The types of material may also provide some changes to ε '. Natural carbonaceous materials usually consist of complex chemical components that could in some way increase or decrease the dielectric properties [2]. Likewise, when the material composition is altered in the pyrolysis process which is irreversible, it generates volatile materials. Generally, the end-product of biomass pyrolysis is rich in carbon content [16]. The carbon content indeed has an important role in the profile of the dielectric properties (through orientation polarization) because of the presence of aromatic rings. The delocalized π -electrons can move freely in a broad region and might ionize their surrounding area [2,8].

In Figs. 3(b, e) and 4(b, e), the ε " of some samples decreased as the frequency was increased at the low frequency region, while at the medium and high frequency regions, the ε " pattern decreased slightly and then plateaued. This might be due to the changes in direct current conductance because ε " is directly proportional to the electrical conductivity. ε " decreases at a low frequency due to ionic conductivity while at a high frequency, it decreases due to bound water relaxation and free water relaxation. The increase of ε " might be due to an increase in the free charge density [15]. PKSK1.75 has the highest loss factor (ε ") which could be related to the higher ratio of K₂CO₃. In contrast, the ε " of PKS-C is higher than that of PKS and the AC-PKSK series. PKS-C has a higher surface area that might influence the value of ε " due to the ample moisture content and high carbon content. The ε " for the AC-PKSK series is in accordance with the amount of moisture. Among the impregnated samples, PKSN2.0 had the lowest ε " which could be due to a smaller moisture content compared to PKSN1.0 and PKSN1.5. Similarly, the increase of the moisture content and the K₂CO₃ ratio resulted in a decrease of the ε " as the frequency was increased.

In contrast, the ε " of the AC-PKSN1.5, AC-PKSN2.0 and PKS-C increased as the frequency was increased probably due to an increase in the free charge density [15].

The profiles of the loss tangent ($\tan \delta$) are shown in the Figs. 3(c, f) and 4(c, f). The pattern of tan δ is similar to that of ε ", but both of them have different attributes; $\tan \delta$ represents the microwave heating efficiency while ε " is used to determine the lossiness of a material and its polarization. From Fig. 3c, PKSK1.75 has a higher value for tan δ compared to the other samples. In Fig. 4c, PKSN1.5 is more efficient to be heated using microwaves followed by PKSN1.0, PKS-C, PKSN2.0 and PKS. A sample with a high tan δ normally has better energy absorption properties, energy storage characteristics and a higher heating rate [11]. The results show that NaOH and K₂CO₃ salts and the moisture content could have some role in enhancing the efficiency of microwave heating. Water is known as a natural polar and prominent absorber in microwaves and has been used as a benchmark for other dielectric materials [5]. However, the patterns of tan δ for all the series are inconsistent with an increasing frequency. This could be associated to the decrease in the interfacial polarization [11] and/or gradual decrease in the dipole movement that produces heat within the material by molecular polarization [2,12].

When compared to the activated samples, the impregnated samples, i.e., PKSK1.75 and PKSN1.5, are good microwave absorbers for microwave-assisted activation due to the high values of $\tan \delta$ ($\tan \delta > 0.1$) even though ε " is <1.0. From the viewpoint of their dielectric properties, PKS and the modified series are categorized as low microwave absorbing dielectric materials (ε " <1.0; $\tan \delta < 0.1$). In general, these samples are not suitable for

microwave-assisted activation, unless an impedance matching (tuning) system is installed between the load and microwave power source to ensure the maximum transfer of power (minimize the reflected power) [8].

3.3. Temperature-dependency of the dielectric properties

Tables 2-4 show the effect of temperature on the dielectric properties of the K₂CO₃- and NaOH-modified samples derived from PKSs at ISM frequencies of 0.915, 2.45, and 5.8 GHz and temperatures of 25, 35, and 45 °C. In general, the ε ' of the PKSmodified samples decreased as the temperature was increased. The nature of ionic solids (salts, NaOH and K2CO3) could affect the ε ' in a temperature-dependent manner. Normally, ionic polarization enhances the ε ' when the temperature increases. At a low temperature, the orientation of the polar dielectrics cannot occur. However, the dipole orientation is facilitated at a high temperature thus increasing the permittivity [17]. The intensified chaotic thermal oscillations of molecules could result in the weakening of the orderliness degree of orientation rendering a maximum ε ' and then suddenly decreasing [17]. Therefore, the ε ' may increase or decrease with temperature depending on the characteristics of the material [5]. The ε increased with the temperature because of the improvement in the ionic mobility of the bound water in the material by reducing the moisture level [5,18]. Consequently, the decrease of the tan δ value depicts a good microwave energy absorption ability of a material [2].

The increase of $\tan \delta$ with the increasing temperature could be a result from the solid impregnation which indirectly signi-

f Table~2. Temperature-dependent, relaxation time and penetration depth of the PKS-modified samples at 25°C												
	0.915 GHz					2.4	45 GHz		5.8 GHz			
Sample	ε'	$\tan\delta$	$\tau(s)$	D_p (cm)	ε'	$ an \delta$	τ (s)	D_p (cm)	ε'	$ an \delta$	τ (s)	D_p (cm)
PKS	3.07	0.010	1.26×10 ⁻⁹	338	2.17	0.040	9.00×10 ⁻¹⁰	36.5	2.25	0.060	1.97×10 ⁻¹⁰	8.72
PKS-C	3.31	0.040	$6.71\!\times\!10^{^{\!-10}}$	72.7	2.80	0.070	3.60×10^{-10}	17.9	2.78	0.100	1.03×10^{-10}	4.98
PKSK0.75	2.80	0.050	3.95×10^{-10}	69.9	2.47	0.060	2.73×10^{-10}	21.0	2.57	0.057	9.69×10^{-11}	9.04
PKSK1.25	3.08	0.020	8.45×10^{-10}	127	2.76	0.030	5.14×10^{-10}	38.1	2.77	0.053	1.23×10^{-10}	9.34
PKSK1.75	3.52	0.160	2.47×10^{-10}	17.5	3.27	0.130	1.64×10^{-10}	8.44	3.07	0.140	8.15×10^{-11}	3.44
PKSN1.0	2.47	0.087	3.05×10^{-10}	38.3	2.21	0.098	1.91×10^{-10}	13.4	2.26	0.104	6.73×10^{-11}	5.25
PKSN1.5	1.87	0.145	3.20×10^{-10}	26.4	1.46	0.117	3.45×10^{-10}	13.8	1.47	0.081	2.08×10^{-10}	8.41
PKSN2.0	2.82	0.046	3.45×10^{-10}	67.4	2.47	0.059	2.75×10^{-10}	21.2	2.57	0.058	9.44×10^{-11}	8.89
AC-PKSK0.75	1.88	0.110	2.84×10^{-10}	35.9	1.66	0.050	4.54×10^{-10}	32.3	1.61	0.030	3.53×10^{-10}	22.4
AC-PKSK1.25	1.91	0.130	2.35×10^{-10}	28.6	1.67	0.060	3.45×10^{-10}	23.3	1.61	0.040	2.88×10^{-10}	17.4
AC-PKSK1.75	1.98	0.070	1.80×10^{-10}	52.0	1.51	0.050	5.18×10^{-10}	31.4	1.51	0.020	5.96×10^{-10}	35.8
AC-PKSN1.0	1.88	0.080	6.02×10^{-10}	44.9	1.76	0.050	4.54×10^{-10}	26.8	1.77	0.060	1.64×10^{-10}	9.83
AC-PKSN1.5	2.74	0.180	5.94×10^{-11}	18.0	2.08	0.110	2.40×10^{-10}	12.7	1.86	0.080	1.85×10^{-10}	7.24
AC-PKSN2.0	1.88	0.036	1.26×10 ⁻⁹	107	1.72	0.056	4.34×10^{-10}	26.5	1.62	0.074	1.72×10^{-10}	8.71
Water	-	-	5.74×10 ⁻¹²	13.4	-	-	8.02×10 ⁻¹²	1.87	-	-	8.29×10 ⁻¹²	0.35

Sample	0.915 GHz					2.4	45 GHz		5.8 GHz				
	ε'	$ an \delta$	τ (s)	D_p (cm)	ε '	$\tan\delta$	τ (s)	D_p (cm)	ε '	$ an \delta$	τ (s)	D_p (cm)	
PKS	2.71	0.029	9.09×10^{-10}	110	2.32	0.047	9.75×10 ⁻¹⁰	27.1	2.30	0.058	1.69×10 ⁻¹⁰	9.31	
PKS-C	2.49	0.024	1.77×10^{-9}	138	2.36	0.043	4.78×10^{-10}	29.8	2.35	0.044	2.01×10^{-10}	12.3	
PKSK0.75	2.42	0.073	6.26×10^{-11}	46.3	2.08	0.091	1.37×10^{-10}	14.9	2.20	0.054	6.33×10^{-11}	10.3	
PKSK1.25	2.21	0.061	3.37×10^{-10}	57.5	1.96	0.067	2.52×10^{-10}	20.8	2.01	0.063	9.79×10^{-11}	9.22	
PKSK1.75	2.28	0.183	8.14×10^{-11}	18.9	1.90	0.145	1.37×10^{-10}	9.79	1.92	0.097	8.26×10^{-11}	6.13	
PKSN1.0	1.69	0.028	3.58×10^{-10}	143	1.22	0.058	6.32×10^{-10}	37.0	1.36	0.040	$2.17{\times}10^{^{-10}}$	17.8	
PKSN1.5	2.57	0.130	9.42×10^{-11}	25.0	2.03	0.147	1.59×10^{-10}	9.30	2.04	0.136	7.05×10^{-11}	4.25	
PKSN2.0	2.61	0.857	3.79×10^{-11}	3.77	2.23	0.504	5.03×10^{-11}	2.59	2.21	0.303	3.66×10^{-11}	1.83	
C-PKSK0.75	2.00	0.030	7.25×10^{-10}	128	1.60	0.040	6.98×10^{-10}	40.9	1.56	0.020	4.91×10^{-10}	26.8	
C-PKSK1.25	1.94	0.079	3.23×10^{-10}	47.4	1.62	0.082	3.00×10^{-10}	18.6	1.57	0.079	1.45×10^{-10}	8.30	
C-PKSK1.75	2.42	0.102	1.36×10^{-10}	32.9	1.69	0.066	5.43×10^{-10}	22.8	1.69	0.047	3.20×10^{-10}	13.4	
AC-PKSN1.0	1.75	0.055	5.13×10^{-10}	72.0	1.58	0.047	3.95×10^{-10}	33.2	1.58	0.055	1.42×10^{-10}	11.9	
AC-PKSN1.5	2.44	0.050	3.40×10^{-10}	63.8	1.97	0.090	2.59×10^{-10}	15.2	1.91	0.120	9.30×10^{-11}	4.90	
AC-PKSN2.0	1.95	0.120	8.38×10^{-11}	31.9	1.54	0.100	2.24×10^{-10}	16.3	1.49	0.050	2.20×10^{-10}	14.3	
Water	-	-	5.54×10^{-11}	16.8	-	-	9.43×10^{-12}	2.30	-	-	7.52×10^{-12}	0.42	

f Table~4. Temperature-dependent, relaxation time and penetration depth of the PKS-modified samples at 45°C												
	0.915 GHz					2.4	45 GHz		5.8 GHz			
Sample	ε'	$\tan\delta$	τ (s)	D_p (cm)	arepsilon '	$\tan\delta$	τ (s)	D_p (cm)	ε '	$\tan\delta$	$\tau(s)$	D_p (cm)
PKS	2.60	0.026	9.36×10 ⁻¹⁰	124	2.24	0.046	4.55×10 ⁻¹⁰	28.4	2.20	0.052	1.65×10 ⁻¹⁰	8.43
PKS-C	2.52	0.019	2.41×10^{-9}	171	2.40	0.042	5.07×10^{-10}	29.8	2.41	0.048	1.86×10^{-10}	12.3
PKSK0.75	2.38	0.034	2.16×10^{-10}	98.8	2.07	0.065	1.97×10^{-10}	20.8	2.23	0.044	$6.82{\times}10^{-11}$	12.5
PKSK1.25	2.44	0.041	4.35×10^{-10}	81.8	2.09	0.058	3.22×10^{-10}	23.3	2.13	0.065	1.11×10^{-10}	8.71
PKSK1.75	2.23	0.261	6.65×10^{-11}	13.4	1.91	0.351	1.02×10^{-10}	7.67	1.90	0.116	6.87×10^{-11}	5.13
PKSN1.0	1.87	0.035	8.53×10^{-11}	108	1.35	0.046	5.76×10^{-10}	36.5	1.46	0.046	1.82×10^{-10}	14.9
PKSN1.5	2.47	0.137	1.12×10^{-10}	24.3	1.91	0.170	1.55×10^{-10}	8.28	1.92	0.150	7.25×10^{-11}	3.95
PKSN2.0	2.11	0.334	1.09×10^{-10}	10.8	1.83	0.254	1.02×10^{-10}	5.67	1.91	0.165	5.63×10^{-11}	3.62
AC-PKSK0.75	1.81	0.030	8.31×10^{-10}	130	1.49	0.042	5.92×10^{-10}	38.2	1.49	0.020	5.28×10^{-10}	33.8
AC-PKSK1.25	1.88	0.072	3.40×10^{-10}	52.5	1.57	0.075	3.20×10^{-10}	20.6	1.53	0.072	1.55×10^{-10}	9.29
AC-PKSK1.75	1.73	0.040	8.09×10^{-10}	98.4	1.48	0.033	7.67×10^{-10}	48.5	1.49	0.034	3.11×10^{-10}	20.0
AC-PKSN1.0	1.75	0.038	1.11×10^{-9}	103	1.61	0.042	5.43×10^{-10}	36.4	1.58	0.055	1.84×10^{-10}	11.9
AC-PKSN1.5	2.62	0.060	2.62×10^{-10}	57.6	2.02	0.100	2.76×10^{-10}	14.3	1.96	0.120	9.96×10^{-11}	4.75
AC-PKSN2.0	1.88	0.120	1.42×10^{-10}	32.8	1.53	0.100	2.31×10^{-10}	16.3	1.49	0.050	2.10×10^{-10}	13.6
Water	-	-	1.33×10 ⁻¹¹	21.1	-	-	2.98×10 ⁻¹²	2.84	-	-	5.92×10 ⁻¹²	0.52

fies the importance of ionic salts (activators) in enhancing the ability of a material to be heated in microwave at elevated temperatures [11,12]. In addition, the ionic conductivity of K⁺ and Na⁺ in the samples (especially at a lower temperature) decreased with the decreasing moisture content and consequently reducing the molecular polarization [7]. While the decrease of tan δ with the increasing temperature observed in the PKS (at 5.8 GHz), PKS-C, AC-PKSN1.0 and AC-PKSN2.0 (at 5.8 GHz), PKSN1.0 (at 2.45 GHz) and K₂CO₃-activated samples are probably due to dipole loss as a result of the evaporation of water when the samples are exposed to a high temperature [12]. It could also be related to the decrease in the interfacial polarization [11] and/or gradual decrease in the dipole movement that produces heat in the material by molecular polarization [2,12]. Nevertheless, the role of NaOH and K_2CO_3 in increasing the tan δ outweighs that of the moisture content.

The interfacial polarization (Maxwell-Wagner polarization) could not follow the variation and respond to the applied field at a low frequency (lower than 2.5 GHz), resulting in no polarization [19]. The Maxwell-Wagner relaxation followed the Arrhenius law which causes the Maxwell-Wagner relaxation to become weaker as the temperature increases [19]. From Tables 2-4, the microwave frequencies of 0.915 GHz and 2.45 GHz are suitable to activate the K_2CO_3 - and NaOH-modified samples because of the reasonably high tan δ . However, other factors such as the capacity of the load, type of processing (continuous/batch), heating rate, technology available, etc. also need to be taken into consideration [8].

3.4. Relaxation time and penetration depth of the PKS-modified samples

Tables 2-4 also summarize the relaxation time (τ) and penetration depth (D_p) of the $K_2CO_{3^-}$ and NaOH-modified samples. In general, the relaxation time (τ) decreased with an increasing frequency because dipoles or molecules try to align themselves along the increasing frequency leading to less polarization [2]. At a low frequency region, polarization is due to dipoles or molecules trying to align themselves as the microwave field slowly rotates. As the frequency increases, a stronger electromagnetic field interferes with the alignment of the dipoles or molecules leading to a partial polarization that slows the relaxation time [11,12]. Subsequently, there is negligible or no polarization hence inefficient heating because of a too rapid microwave field at a high frequency.

In this work, multiple slopes that correspond to the number of relaxation times were obtained at varying frequencies. This deviates from a linear, single relaxation of the Debye equation [2]. This could be due to the homogeneity of the samples; PKS and PKS-C are homogenous, while the K₂CO₃- and NaOH-modified samples are heterogeneous. Normally, the heterogeneous material deviates from the Debye relaxation and produces multiple relaxations. In addition, the relaxation time also depends on the size of the molecules and intermolecular forces between the molecules [12]. Thus, it is assumed that the relaxation time can also be related with the structure and homogeneity of the material.

The relaxation time decreased with the temperature because there is no or less polarization at a high temperature [2]. The relaxation time becomes shorter due to the increase of the molecular collision and randomization rate during the heating process [20]. When heat from a water bath is transferred to a sample, it provides energy to molecules (dipoles) to become energetic. As a result, the molecules need less time to become 63% oriented in the electric field [20].

From Tables 2-4, the penetration depth (D_p) of the K_2CO_3 modified samples decreased as the frequency was increased. However, the NaOH-modified samples showed an undefined pattern for the D_n with the temperature. As the frequency increases, the electromagnetic energy is more inclined towards the nearest surface of the material that can cause a short distance of penetration [2,11]. PKSK1.25 shows a decrease in D_n after activation. In Table 3, at 35°C and a frequency of 0.915 GHz for example, the value of D_n decreases from 57.5 cm to 47.4 cm. This could be linked to the carbon content of the AC-PKSK1.25 (88.5% carbon) which improves the lossiness of the material and thus increases its propensity to dissipate heat. On the other hand, AC-PKSN2.0 has a D_n of 31.9 cm, which increased from 3.77 cm before the activation. It signifies that the material becomes less lossy (transparent) upon activation, which is probably due to a high ash content (73.4%) and a decreased carbon content. The decrease of D_p is generally attributed to the effect of the loss factor (ε "); a sample with a high capability to convert electromagnetic energy (high loss material) into heat tends to have a low penetration depth [1]. A low loss material, on the other hand, is known to have a relatively low ε ", but a large distance for D_p . A longer penetration depth is favorable for uniform and effective microwave heating.

Furthermore, moisture content and carbon content can also influence the microwave penetration depth into a material. From Tables 2-4, water has the lowest penetration depth as the frequency increases even though it is a polar dielectric and good microwave absorber. When moisture is present in a material, the penetration depth is only centered on the material surface where the moisture is normally accumulated because ε and ε are relatively high [21]. However, when the carbon content and/or ionic solids (K₂CO₃ and NaOH) are present together with moisture, the penetration depth can be far from the material surface to a certain extent. For example, the D_p of AC-PKSN1.0 is higher than that of AC-PKSN1.5 and AC-PKSN2.0 because of a low moisture content and a high carbon content.

3.5. Correlations between the dielectric properties and material characteristics

Fig. 5 shows the relationship between the carbon content and dielectric properties. The samples with a high carbon content generally have high values of ε ' and $\tan \delta$. According to Salema et al. [2], aromatic carbons in the activated samples develop a high polarization due to the delocalized π -electrons that freely move hence ionizing the surrounding area. For materials with a carbon content lower than 85%, the ε ' seems to show a fluctuating trend because of a possible influence by the moisture content that is higher than 10% and also the ash content that is more than 20%. Additionally, the $\tan \delta$ increased with the carbon content. A good microwave absorber normally has a high ε " and $\tan \delta$ (ε " >1.0, $\tan \delta$ >0.1). However, other associating factors such as the moisture content and types of materials (the presence of ash and

ionic solids) also have some role in the dielectric properties [10].

Fig. 6 shows the relationship between the carbon content and the penetration depth. The penetration depth presumably increased with increasing carbon content. For materials with a high carbon content, multiple values for the penetration depth could be obtained due to the presence of moisture. Hence, a carbonaceous material that has a high moisture content would not be heated thoroughly because of the shorter penetration depth because the hotspots are mainly centered on heating the moisture [7]. From Fig. 6, some materials with a low carbon content (<80%) also show a high D_p due to a low amount of moisture. Likewise, some materials with a high carbon content (>80%) have a low D_p due to a high moisture content. The activated samples with a high surface area could accommodate more moisture and had a shorter penetration depth despite their high carbon content

Fig. 7 shows the correlation between (a) the specific surface area and (b) the moisture content and the dielectric properties. In Fig. 7a, the dielectric properties are slightly improved for the activated samples with a high surface area. Material with a low surface area deviated from this trend due to a low moisture content (0.36%), while material with a high surface area is affected by a high moisture content (17%) but a low carbon content (31.8%). The tan δ also shows an indirect correlation

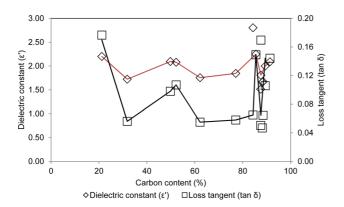
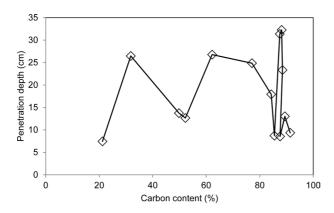


Fig. 5. Relationship between the carbon content and the dielectric properties.

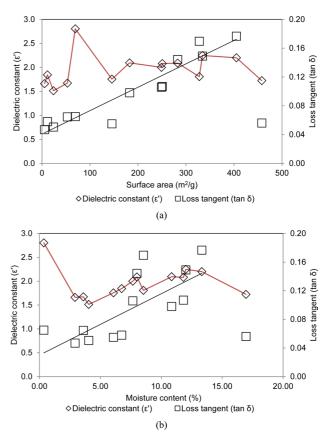


 ${f Fig. \ 6.}$ Relationship between the carbon content and the penetration depth.

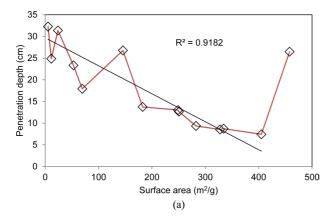
with the carbon content; a low $\tan \delta$ of material with a high surface area might be due to a low carbon content. It can be concluded that the surface area could offer a positive effect on the dielectric properties. Moreover, associated factors such as the moisture content and the carbon content enable a material to dissipate the electromagnetic energy into heat and thus potentially can be used in microwave-assisted activation. From Fig. 7b, the dielectric properties are directly attributed to the moisture content. Samples with a sufficient amount of moisture and a high carbon content have high values for ε '. Similarly, materials with a high moisture content (17%) and a low carbon content have a moderate ε ' and $\tan \delta$. Moisture (water) is a natural polar dielectric that can polarize with the electromagnetic field for effective microwave heating [2].

Fig. 8 shows the relationship between (a) the surface area and (b) the moisture content and the penetration depth. From Fig. 8a, the penetration depth D_p decreased with an increasing surface area. A negative slope was obtained with a R²=0.92, suggesting that the surface area has an inverse response to the penetration depth because of a high moisture content and that the electromagnetic wave would only attack a surface laden with moisture.

The penetration depth linearly decreases as the moisture content increases shown in Fig. 8b. The carbonaceous samples with a high moisture content would not be heated thoroughly because the penetration depth is shorter as a result of the hotspots that are



 ${\bf Fig.}$ 7. (a) Relationship between the surface area and the dielectric properties and (b) relationship between the moisture content and the dielectric properties.



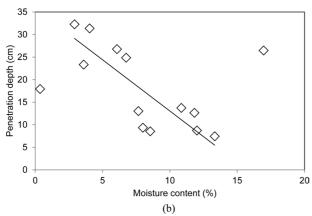


Fig.~8. (a) Relationship between the surface area and the penetration depth and (b) relationship between the moisture content and the penetration depth.

mainly centered in heating the moisture on the material surface [7]. The disparity and interplay between the effects of the moisture content on the dielectric properties (ε " and $\tan \delta$) and the D_p thus necessitate the need for multiple operating frequencies in microwave-assisted activation to accommodate the changes in the material characteristics so to ensure the desired end-product quality through effective and thorough heating.

4. Conclusions

Palm kernel shells (PKSs) were modified using potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH) at three different ratios. The dielectric properties of the modified samples are influenced by the frequency, temperature, activating agents (ionic solids), moisture content and carbon content. Under a frequency-dependent condition, a high ε ' and tan δ could be associated with a high moisture content and carbon content for a better microwave-assisted activation. However, the declining pattern of tan δ at a high temperature for all the samples is due to the decrease in the moisture content and free water. Besides, the material characteristics and conditions could also have some role in the pattern for the dielectric properties. Carbon content, moisture content, amount of ionic solids and surface area all showed direct relationships with the dielectric properties and the

penetration depth. The penetration depth increased with increasing carbon content, while it decreased with increasing surface area. This is in agreement with the fact that a material with a high surface area may also exhibit a high moisture content. Because of these varying properties with the changes in material characteristics from impregnation to activation, it is therefore imperative to select a suitable frequency or multiple frequencies in microwave-assisted activation.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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