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Dielectric Properties of Sodium Hydroxide-Impregnated and Activated Cempedak Peel Samples at Microwave Frequencies

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This study was aimed to evaluate the dielectric properties of sodium hydroxide-impregnated samples and activated carbons derived from jackfruit peel (Artocarpus chempeden, Artocarpus integer). The dielectric properties were examined by using open-ended coaxial probe method at microwave frequencies. The results show that the dielectric properties of cempedak peel samples are influenced by frequency, concentration of activator, moisture content and carbon content. The impregnated sample with NaOH ratio of 1.5 (CN1.5) showed a better microwave absorber due to sufficient moisture content (8.55 %), consequently higher tan δ. Sodium hydroxide can function as microwave absorber to enhance the efficiency of microwave heating for low loss material like cempedak peel. Moisture content and carbon content have to be taken into consideration as these parameters can influence the dielectric properties of the modified cempedak peel samples.

1. Introduction

Cempedak (Artocarpus chempeden, Artocarpus integer) is a local fruit that can be found in south Asia and Australia. Cempedak flesh is edible and can be consumed fresh or after being processed. The inedible parts of cempedak (e.g., peel, straw, etc.) comprise about 50 % to 75 % of the fruit are usually discarded as waste (Subhadrabandhu, 2001). The skin of breadfruit (Artocarpus altilis) (Lim et al., 2014), cempedak durian (Artocarpus integer) (Dahri et al., 2015) and breadnut (Artocarpus camansi) (Chieng et al., 2015) have been converted into activated carbon for the removal of dyes and heavy metals from water. It shows that cempedak peel is a candidate of activated carbon precursor. Focus has been directed to microwave heating as a promising alternative to conventional heating in activated carbon preparation. Dielectric properties of materials are often neglected in microwave-assisted activation, even though they are crucial in microwave heating mechanisms (Sosa-Morales et al., 2010). The efficacy of microwave heating is associated with the dielectric properties of material to be heated. The dielectric properties are important in order to define the interaction between electromagnetic field and material to achieve uniform heating and good end-product quality through sufficient penetration depth of microwave energy (Motasemi et al., 2014). There are still limited information with regard to the dielectric properties of cempedak peel, especially when microwave is employed for heating and activation. This study was aimed to evaluate the dielectric properties of cempedak peel and its sodium hydroxide-impregnated and activated samples. The effects of frequency and impregnation ratio on dielectric properties were discussed and suitable microwave operating conditions for activation were proposed.

2. Materials and methods

2.1 Samples Preparation

Cempedak peel (CP) was obtained from local market. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) are of analytical reagent grade and were purchased from Merck and R&M chemicals. 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

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500 µm. About 20 g of CP was mixed with different ratios of NaOH (1.0, 1.5 and 2.0) based on weight of sodium hydroxide per weight of precursor. 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 designated as CN1.0, CN1.5 and CN2.0.
The impregnated samples were activated using furnace at 500 °C for 2 h, and the activated carbons were labelled as AC-CN1.0, AC-CN1.5 and AC-CN2.0. The activated carbons were washed with 0.9 M HCl and then rinsed thoroughly with distilled water to a constant pH. The cempedak peel char (CC) was obtained through pyrolysis of CP in furnace at the same conditions.

2.2 Samples characterisation

Moisture content is the percentage of free water or moisture in the materials. The moisture content (dry basis) was calculated as (w_i-w_d) x 100/w_d, where w_i is the initial mass of sample, and w_d is the mass of sample after oven-dried for 24 h at 110 °C. Ash content is the amount of minerals or leftover when the volatiles and organic matters are removed at 800 °C for 2 h. Ash content was calculated as w_f x 100/w_d, where w_f is the mass of ash. The ash content was only determined for CP precursors.
Carbon content of the materials was obtained by using EDX (Oxford Instrument). The dielectric properties were measured at various frequencies (1 to 6 GHz) using open-ended coaxial probe technique. The measurement system consists of coaxial probe (HP 85070D) attached to a Vector Network Analyser (VNA model HP 8720B). The measurement of each sample was repeated at least for 5 times to ensure good reproducibility of results (Kamaruddin et al., 2014a).

3. Results and discussion

3.1 Characteristics of samples

Table 1 shows the characteristics of NaOH-impregnated samples and activated carbons derived from cempedak peel. CN1.0 shows the highest moisture content compared to other samples, and the of moisture content decreased as the ratio of NaOH increased for the impregnated samples. AC-CN2.0 contains a higher amount of moisture when compared to the other two activated carbons. The amount of NaOH is related to the increase of moisture content because of the increase of specific area of activated carbons. The bigger the pore volume, the more the water vapour that can be readily adsorbed by activated carbon. AC-CN2.0 has higher ash content, followed by AC-CN1.5, AC-CN1.0, CC and CP. The presence of high ash content could be originated from the use of NaOH in activation.

Table 1: Characteristics of NaOH-impregnated samples and activated carbons derived from cempedak peel

Sample	Moisture content (%)	Ash content (%)	Carbon content (%)	Yield (%)	Surface area (m^2/g)
CP	12.8	6.50	57.4	-	-
CN1.0	14.9	-	-	-	-
CN1.5	8.55	-	-	-	-
CN2.0	4.99	-	-	-	-
AC-CN1.0	10.9	42.0	49.8	21.0	183
AC-CN1.5	12.0	70.4	85.5	33.9	334
AC-CN2.0	13.3	83.3	21.2	79.1	405
CC	6.75	11.8	77.1	32.5	11.4

From Table 1, the order of carbon content in samples is, AC-CN1.5 > CC > CP > AC-CN1.0 > AC-CN2.0. The yield of activated carbons increased as the ratio of NaOH increased and beyond ratio 1.5 (optimum), the carbon content might decrease due to excessive use of NaOH. However, the ash content also increased. It indicates that activating agent (NaOH) chaotically decomposes the volatiles in cempedak peel, thus decomposing the carbon content. The boiling point of NaOH is higher (1,388 °C) than the activation temperature (500 °C), so it probably remained after the activation. Surface area is crucial to define the effectiveness of activated carbon in adsorption process. From Table 1, the surface area increased when the ratio of NaOH increased. The values are 183, 334 and 405 m^2/g for AC-CN1.0, AC-CN1.5 and AC-CN2.0.

3.2 Effect of frequency on dielectric properties

Dielectric properties (or permittivity) is expressed as Eq(1),

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad (1)$$

where ε' is the dielectric constant (real part of permittivity), a measure of how much energy from an external electric field can be stored within a material through polarisation mechanism, while ε" is the loss factor (imaginary part of permittivity) that defines the ability of material to absorb and dissipate the electromagnetic energy into heat. Tan δ is used in defining how efficient the electromagnetic energy stored within a material is converted into heat at specific frequency and temperature. It is given as Eq(2) (Kamaruddin et al., 2014b):

$$\tan\delta = \varepsilon''/\varepsilon' \quad (2)$$

The dielectric properties aids in scrutinising microwave heating and material interaction, predicting heating rates, and describing heating characteristics and behaviour of material when subjected to high-frequency electromagnetic fields (Venkatesh and Raghavan, 2004).
Penetration depth, D_P is useful to determine how far electromagnetic power can go inside a material, and it is given as Eq(3) (Hesas et al., 2013),

$$D_P = \frac{\lambda_o\sqrt{\varepsilon'}}{2\pi\varepsilon''} \quad (3)$$

where λ_o is the free space microwave wavelength (for 2.45 GHz, λ_o = 12.2 cm). The volumetric heating is presumably less operative for a material with short penetration depth when only small portion of material thickness absorbs the microwave. Heating becomes not uniform due to poor strength of electromagnetic wave at material core that farther the value of penetration depth (Kim et al., 2014).
Figures 1 and 2 represent the effects of frequency on dielectric properties of NaOH-impregnated samples and activated carbons at room temperature. Figures are divided into three parts which are low, medium and high frequency regions. The values of dielectric properties (ε', tan δ and D_P) at ISM frequencies are summarised in Table 2.
In general, the patterns of ε', ε" and tan δ decreased with increasing frequency. Figure 1(a) shows an inconsistent behaviour of ε' because of Maxwell-Wagner polarisation and/or ionic conduction. A little movement of charges at higher frequency consequently results in the alignment of charge dipoles (Zaini et al., 2015). At low frequency regions, the ε' is affected by the presence of moisture in the sample (Omar et al., 2011). While the decrease of ε' as the frequency increased could be due to polarisation at varying electric field (Salema et al., 2013). The ε' of CP and CC are higher than that of NaOH and NaOH-impregnated samples (except for CN1.5). It implies that the NaOH-impregnated samples (except for CN1.5) can store less energy than CP and CC. The dielectric properties of CN1.5 shown in Figure 1(d) are higher compared to the other impregnated materials. CN1.5 is more effective to store more energy from an external electric field through polarisation mechanism.
Figure 2(a) shows a decreasing trend of ε' at low frequency region. The Maxwell-Wagner polarisation seems to prevail at low frequency region for all NaOH-impregnated samples and activated carbons. The inconsistency of ε' at higher frequency regions might because of polarisation tries to align with the varying frequencies. Among the NaOH-activated cempedak peel carbons, AC-CN1.5 exhibits a higher value of ε', followed by AC-CN2.0 and AC-CN1.0. This happens due to high carbon content with sufficient amount of moisture content. The moisture content is directly proportional to dielectric polarisation (Ling et al., 2015).

Table 2: Dielectric properties of cempedak peel samples at ISM microwave frequencies at room temperature

Sample	0.915 GHz			2.45 GHz			5.80 GHz		
	ε'	tan δ	D_p	ε'	tan δ	D_p	ε'	tan δ	D_p
CP	2.44	0.03	123	1.92	0.05	31.3	1.98	0.06	9.25
CC	2.27	0.04	82.1	1.85	0.06	24.9	1.82	0.07	8.75
CN1.0	1.11	0.10	99.8	1.78	0.04	25.0	1.41	0.07	11.4
CN1.5	18.4	1.07	1.83	15.41	0.73	1.13	12.6	0.49	0.64
CN2.0	1.19	0.44	23.7	1.73	0.17	13.8	1.33	0.12	8.07
AC-CN1.0	2.80	0.09	33.2	2.09	0.10	13.7	1.98	0.11	5.30
AC-CN1.5	3.01	0.16	18.9	2.25	0.15	8.72	2.09	0.15	3.87
AC-CN2.0	2.91	0.19	16.0	2.20	0.18	7.44	2.03	0.16	3.60

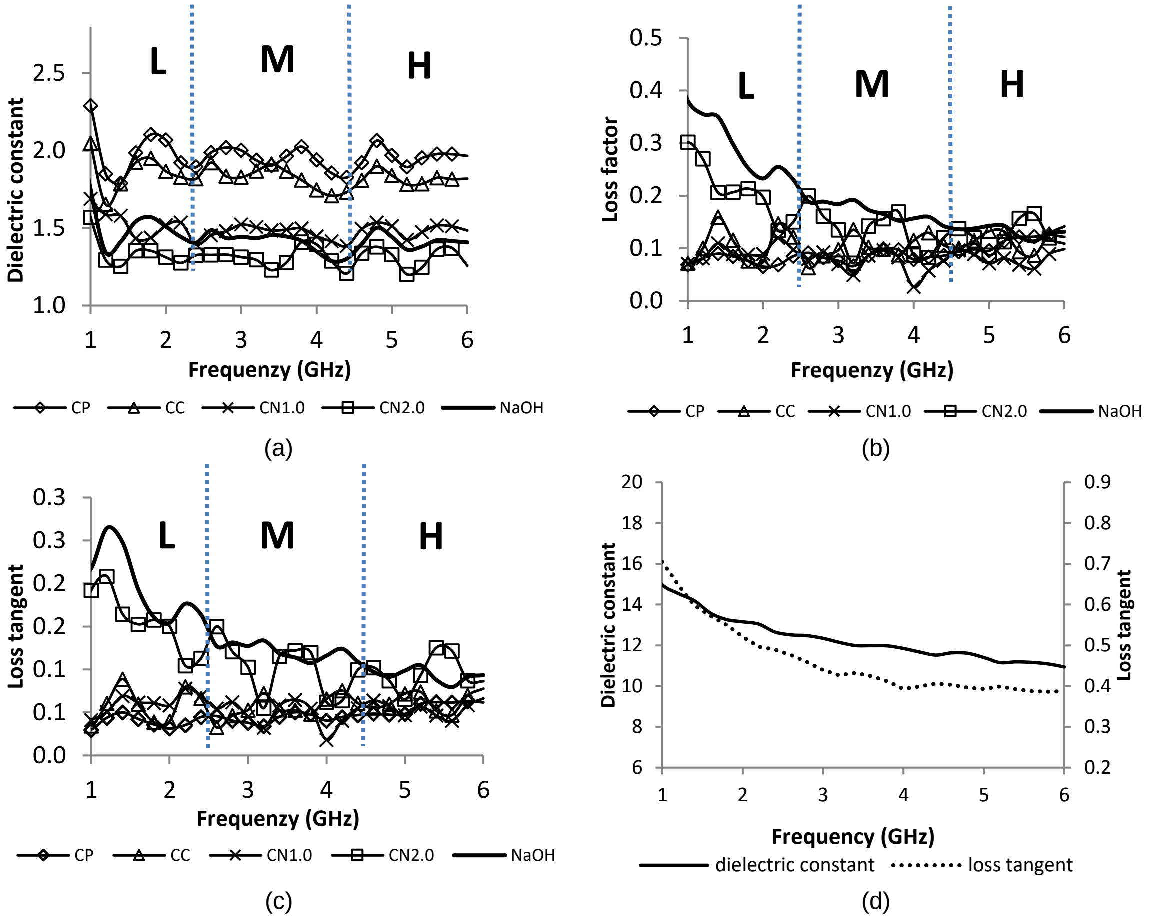

Figure 1: Effect of frequency on dielectric properties, a) dielectric constant b) loss factor c) loss tangent d) dielectric constant and loss tangent of CN1.5, for NaOH-impregnated cempedak peel samples at 25 °C

Figures 1 (b) and 2 (b) show the effect of frequency on the loss factor (ε”) of materials. From a bigger view, the ε” of CN1.5, CN2.0 and NaOH decreased as the frequency increased. While no significant changes were observed for CC, CP and CN1.0. This phenomenon could be due to ionic conduction that is dominant at low frequency region, and bound water and water relaxations at high frequency regions (Venkatesh and Raghavan, 2004; Salema et al., 2013). Figure 2(b) shows a decreasing pattern of ε” of the activated carbons at low and high frequency regions, and there is an increasing trend at medium frequency region. For activated carbon series, AC-CN2.0 gave a higher ε”, followed by AC-CN1.5 and AC-CN1.0 due to high ratio of NaOH with sufficient moisture content and carbon content. From Table 1, the moisture content increased as the ratio of NaOH increased for activated carbon series. It signifies that the ε” increased as the moisture content increased because the material with sufficient moisture content has much ability to convert electromagnetic energy into thermal energy (Sosa-Morales et al., 2010). The increase of salt (NaOH) content in the impregnated samples also enhances the ε” (Sosa-Morales et al., 2010).

The loss tangent (tan δ) of NaOH-impregnated samples and activated carbons are shown in Figure 1(c) and 2(c). The behaviour of tan δ of the samples is similar with that of ε” previously discussed in Figure 1(b) and 2(b). But their function is different as tan δ is about how efficient the material to convert electromagnetic energy into heat while ε” is used to determine the lossyness of the material and its polarisation. From Figure 1(c), it shows that CN1.5 possesses the highest tan δ compared to other samples. CP and CN1.0 have higher moisture content than CN1.5, but CN1.5 exhibits a better tan δ. It can be summarised that sufficient amount of moisture content and moderate ratio of NaOH could play a crucial role in dielectric properties. This happen might be due to the influence of NaOH as activating agent in impregnation and activation is expected to promote high value of tan δ. AC-CN2.0 displays a higher tan δ, followed by AC-CN1.5 and AC-CN1.0. As the ratio of NaOH increases, the moisture content also increases because of the increase in surface area thus making the tan δ increases as well. All NaOH-activated cempedak peel carbons are suitable to be heated using microwave as the tan δ values are more than 0.1 even though the ε” values are lesser than 1.0 that

indicate they are low loss material. From the viewpoint of microwave-activation, only CN1.5 and CN2.0 demonstrate a promising ability to convert the electromagnetic energy into heat at low frequency region.
From Table 2, the penetration depth decreased as the frequency increases for all samples. As the frequency rises, the electromagnetic energy is more inclined towards the nearest surface of the material that can cause a short distance of penetration (Salema et al., 2013). A higher penetration depth is favourable for uniform and effective microwave heating. The moisture content and carbon content can also influence the microwave penetration depth into the material. When the moisture is present, the penetration depth is only centred on the material surface where the moisture is normally accumulated (Komarov et al., 2005). When the carbon content and/or NaOH salt are present along with the moisture, the penetration depth can be far and deeper from the material surface to a certain extent.

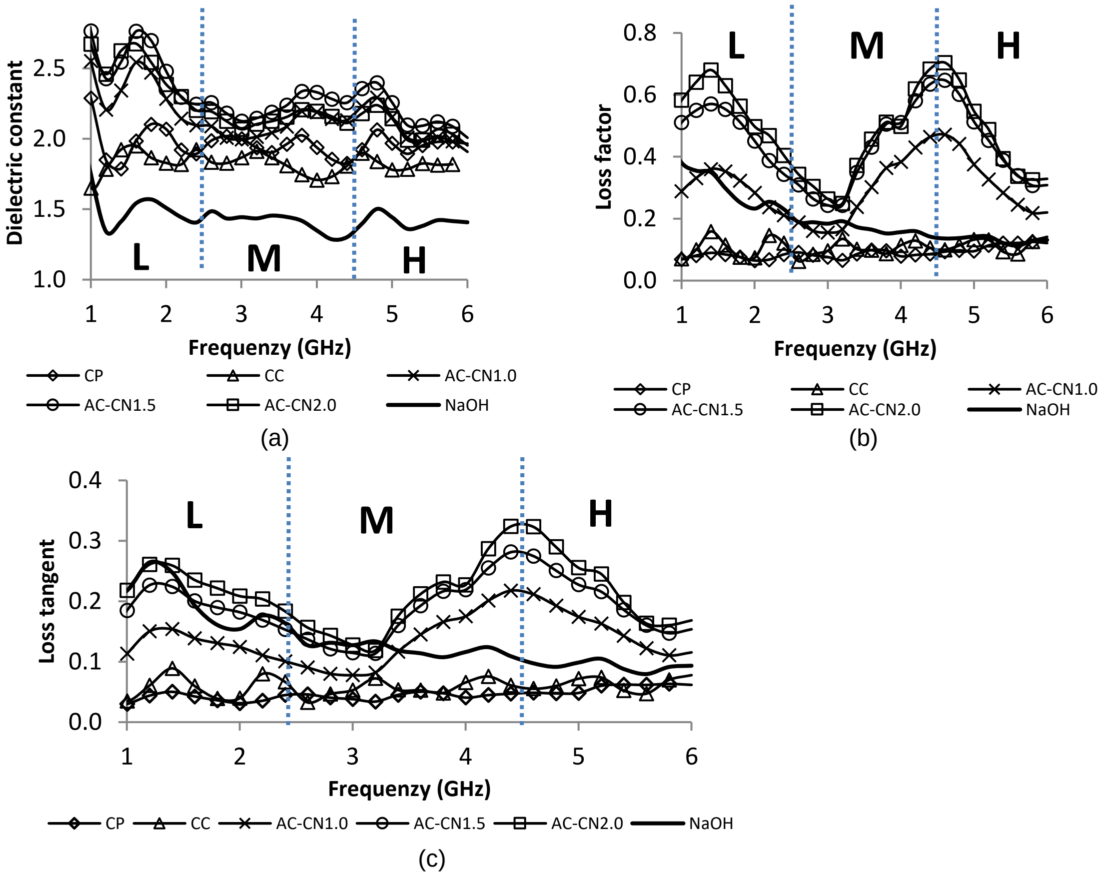

Figure 2: Effect of frequency on dielectric properties, a) dielectric constant b) loss factor c) loss tangent, for cempedak peel-based activated carbons at 25 °C

4. Conclusion

The dielectric properties of NaOH-modified cempedak peel samples are influenced by frequency, concentration of activator, moisture content and carbon content. In frequency-dependent, CN1.5 is a better microwave absorber because it possesses a higher tan δ due to moisture content as compared to other NaOH-impregnated CP. Meanwhile AC-CN2.0 shows a better microwave absorber due to high content of moisture (13.3 %) and sufficient carbon content as compared to the other two activated carbons. The attentive of NaOH as activating agent in impregnation and activation is expected to become a microwave absorber and offer a higher tan δ. Ionic activating agent used in this work, NaOH functions not only as activating agent but also as microwave absorber to enhance the efficiency of microwave heating of low loss material of cempedak peel. The penetration depth is affected by NaOH salt, the carbon content and moisture content to a certain extent. It seems that 2.45 GHz is suitable for microwave-assisted activation of cempedak peel samples as it gives a reasonably higher value of tan δ.

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