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Composition- and Temperature-Dependent of Dielectric Properties of Zinc Chloride-Palm Kernel Shell Mixture at Microwave Frequencies

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Abstract: This work aims to evaluate the composition and temperature dependent of dielectric properties of activated carbon precursor mixture in microwave-assisted chemical activation. Varying fractions of zinc chloride solution and palm kernel shell were used, and the dielectric properties were determined using open-ended coaxial probe method at microwave frequencies. Results show that the dielectric constant, ε'_r decreased with increasing frequency and electrolyte concentration. Results also suggest that mixture containing higher electrolyte concentration is suitable to be heated under microwave at lower frequency. In addition, the loss tangent, tan δ and penetration depth, D_p are slightly improved at higher temperature. Suitable selection of frequency is therefore imperative for effective heating by microwave as the composition and temperature are also dependent on the dielectric properties.

Key words: Char, dielectric properties, microwave-assisted chemical activation, palm kernel shell, penetration depth, zinc chloride.

1. Introduction

The use of microwave in chemical synthesis has been increasingly popular over the last few years [1], [2]. Microwave heats the material from the inner of the material and gradually expanding the heating to the surface [1]. Compared to the conventional heating method, microwave heating has advantages of reducing processing time, uniform and selective heating, high heating rate, and no direct contact between the heating source and the material to be heated [3]. Heating via microwave is possible when the material is able to absorb the microwave, or simply known as microwave absorbers [4].

Microwave heating depends largely on the dielectric properties of the material. It represents the behaviour of the material when it is subjected to the microwave field [3], [4]. Dielectric properties are vital in understanding the response of a material to microwave especially when it comes to the scaling up and design of microwave applicator for mass production [3]. Failure to understand these important characteristics would inevitably lead to the non-reproducible and poor quality of the products [5], [6].

One of the promising application of microwave heating is in the chemical synthesis of activated carbon [7]. Two important materials for the production of activated carbon are carbonaceous precursor and chemical activator [8]. However, the dielectric properties of the individual materials and also the mixture involved in the process were not clearly reported and discussed in much of published literature [3]. Moreover, most reports focuses on the use of domestic microwave (2.45 GHz), and such outcomes would not be applicable for other microwave frequencies [9]. Therefore, this work was aimed at evaluating the dielectric properties of the precursor material and its impregnated mixtures at different microwave frequencies, compositions and temperatures. The results are expected to shed some light on the behaviour of materials in the production of activated carbon via microwave-assisted chemical activation.

2. Materials and Methods

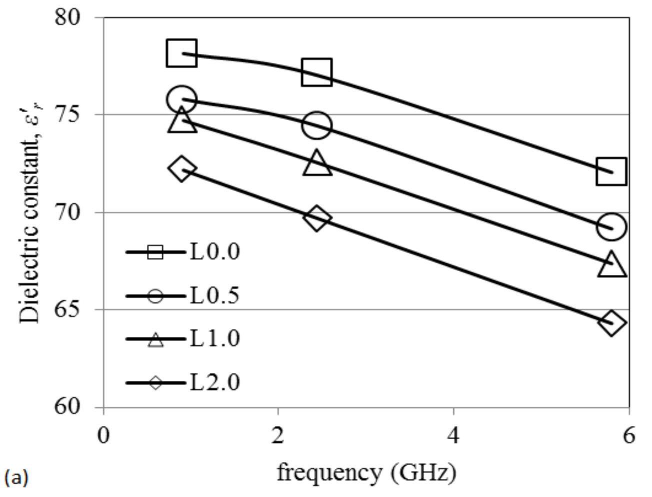
Palm kernel shell (PKS; characteristics C: 50%, H: 5.6%, N: 0.72%, O: 35%; ash: 1.3%; moisture: 8.5%) was obtained from FTA palm oil mill, located at Johor state of Malaysia. PKS was used as the carbonaceous precursor for activated carbon. Analytical-reagent grade zinc chloride ($ZnCl_2$) was purchased from R&M Chemicals.

Palm kernel shell was ground to an average uniform size of 0.6 mm, and was mixed with $ZnCl_2$ in 50 mL distilled water at dried mass ratios ($ZnCl_2$:PKS) of 0:1, 0.5:1, 1:1 and 2:1. These samples hereinafter are designated as L0.0, L0.5, L1.0 and L2.0, respectively. Then, the solid-in-liquid mixtures were dried (impregnated) in microwave oven for 20 minutes. The resultant materials were washed with distilled water to a constant pH, and were oven-dried overnight prior to be used. The solid char/impregnated samples were referred as S0.0, S1.0 and S2.0, respectively.

The dielectric properties of the materials were determined at varying operating frequencies and temperatures. The dielectric properties were measured using Keysight 85070E dielectric probe (Formerly Agilent Technologies) attached to the Keysight E5071C network analyzer from 1 to 6 GHz. The temperature of the samples was adjusted using hot plate between 25 and 45^{o}C. The dielectric probe aperture was immersed into the solid-in-liquid samples or pressed to the solid samples prior to measuring the dielectric properties. The measurement was repeated for five times to obtain the average values.

3. Results and Discussion

3.1. Composition-Dependent of Dielectric Properties



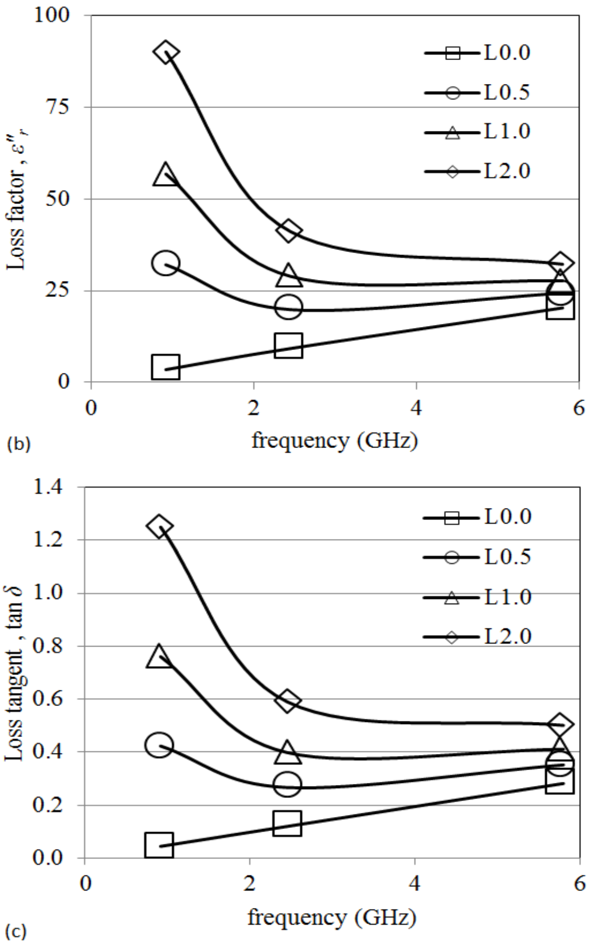


Fig. 1. Effect of frequency on dielectric properties of zinc chloride-palm kernel shell mixture.

Fig. 1 shows the effect of frequency on the dielectric properties of zinc chloride-palm kernel shell mixture. In Fig. 1(a), the dielectric constant, ε'_r dominates at low frequency and decreased significantly as the frequency increases. The dielectric constant, ε'_r determines the behaviour of the material under microwave radiation. It includes how much energy is reflected from the material, as well as how efficient is the material to store the microwave energy. The decrease in ε'_r with increasing frequency is probably due to the gradual decrease in the dipole (water molecule) movement or change in its orientation. This is because the dipoles need to try aligning themselves with rapidly varying electric field of the electromagnetic waves. Such interaction causes the heating in the material. From Fig. 1(a), it is obvious that the composition of zinc chloride in the mixture alters the ε'_r of the material. The ε'_r values were found to be decreased as the fraction of zinc chloride increased. This could be associated with the presence of zinc cations that reduces the dipoles potential [10].

In Fig. 1(b), the loss factor, ε''_r for materials under studied also exhibits a decreasing trend from low frequency and slowly becoming stable at a higher frequency, except for sample L0.0 (palm kernel shell in water). The loss factor, ε''_r represents the ability of the material to absorb and convert electromagnetic energy into heat, and it is also a measure of the heat (energy) released from the material. The loss factor, ε''_r is directly proportional to the electrical conductivity, σ of material, and it increased with increasing the concentration of electrolyte ($ZnCl_2$). Thus, the decreasing trend, L2.0 > L1.0 > L0.5 > L0.0 is likely due to the σ change in the mixture. The presence of dipoles in the conductive mixture allows it to be heated via microwave [11].

The loss tangent, tan δ describes the ability of a material to dissipate the stored energy (microwaves) as heat, and is given as,

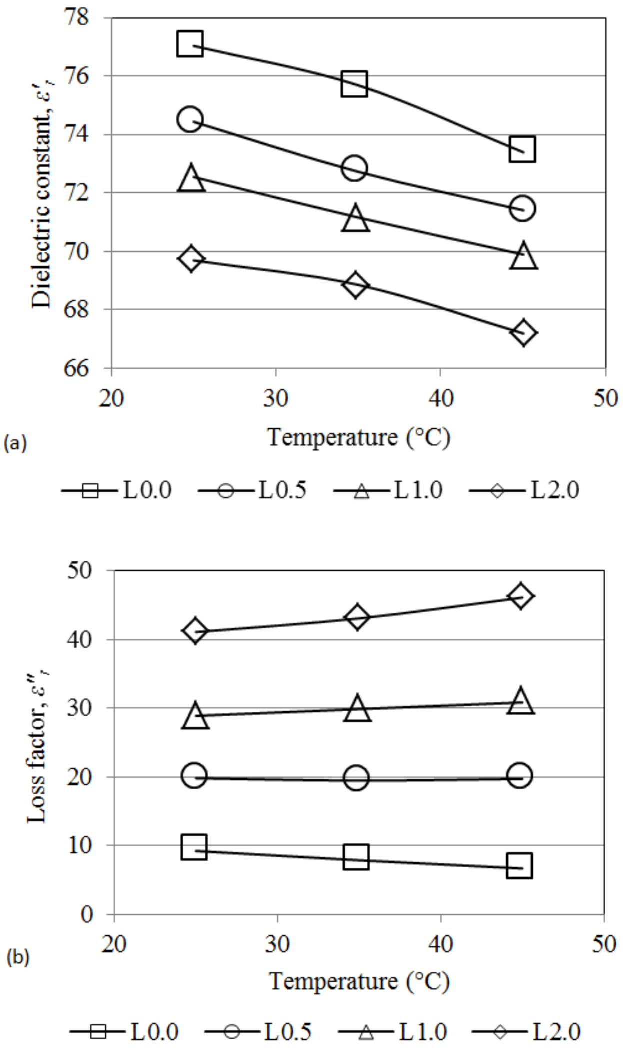
$$\tan\delta = {\varepsilon''_r}/{\varepsilon'_r} \tag{1}$$

From Fig. 1(c), it shows that the loss tangent, tan δ is largely dependent on the loss factor, ε''_r. It implies that the ability of material to be heated under microwave is reduced if it goes beyond the right frequency. Therefore, the microwave frequency cannot be too low or too high in order to achieve efficient heating.

As the fraction of $ZnCl_2$ increased, the tan δ increased while the ε'_r decreased due to increase of electrolyte concentration. It indicates the greater presence of the conductive charge carriers that will also increase the loss system due to charge migration. It also implies that the microwave absorption of electrolyte mixture is more efficient at a lower frequency. While the power absorption and heating rate of the non-electrolyte sample (L0.0) is better and faster at a higher frequency.

4. Temperature-Dependent of Dielectric Properties

Fig. 2 shows the effect of temperature on dielectric properties of zinc chloride-palm kernel shell mixture at 2.45 GHz. In Fig. 2(a), the dielectric constant, ε'_r for all materials exhibits a decreasing trend with the increase of temperature. This might due to the polarization taking place in the heated mixture [12].



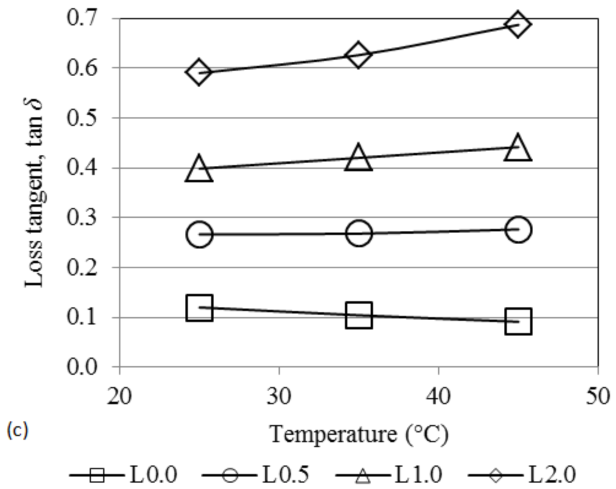


Fig. 2. Effect of temperature on dielectric properties of zinc chloride-palm kernel shell mixture at 2.45 GHz.

Both loss factor, ε''_r and loss tangent, tan δ display a slight increasing trend for electrolyte mixture as the temperature increases. It can be possibly considered that such increase is an outcome of the ionic conductivity at higher temperature [13]. At relatively high temperature, the bond charge carriers get enough excitation thermal energy to obey the change in the external field more easily. Space charge contribution to the polarization may also be attributed to the electrolyte concentration. This enhances the polarization leading to an increase of dielectric behaviour at higher temperature. It suggests that the ability of material to absorb microwave energy at higher temperature is more stable with the presence of electrolyte. Also, it elucidates the dependence of temperature and electrolyte concentration on dielectric properties at the fixed frequency.

5. Dielectric Properties of Char

Table 1 shows the dielectric properties of char materials at different temperatures and microwave frequencies.

Table 1. Temperature and Frequency Dependent of Dielectric Properties of Char

Sample	0.915 GHz		2.45 GHz		5.81 GHz	
	ε'	tan δ	ε'	tan δ	ε'	tan δ
25°C						
S0.0	2.05	0.0243	1.99	0.0406	2.10	0.0428
S1.0	2.05	0.0208	1.93	0.0401	2.05	0.0762
S2.0	2.45	0.0260	2.31	0.0440	2.42	0.0482
45°C						
S0.0	1.97	0.0191	1.84	0.0432	1.97	0.0393
S1.0	2.59	0.0163	2.18	0.0417	2.29	0.0460
S2.0	2.10	0.0112	1.94	0.0435	2.09	0.0387

At 0.915 GHz, the loss tangent, tan δ was found to decrease with increasing temperature from 25 to 45°C. This could be explained by the dipole loss resulting from the rotation of water molecules in the solid samples. It is associated with the release of moisture when the material was heated at higher temperature (moisture content of solid materials under studied at 25°C, ca. 8.5%). The influence of temperature on the solid dielectric properties is not consistent as it depends on the applied frequency, material composition and moisture content [14]. For the two temperatures examined, the values of tan δ increased with increasing frequency. This is probably due to the delocalization of π electrons in the aromatic structures of char materials that facilitates the ability for the material to be heated-up under microwave [3], [15].

From Table 1, the solid materials demonstrate lower values of ε'_r and tan δ than their L-series counterparts. It gives a clear indication that water and electrolytes are better loss materials for microwave. The variation in the dielectric properties of the solid materials infers that suitable frequency should be employed for effective heating so as to obtain the desired quality of activated carbon, and therefore should be considered in the design parameters of microwave applicator.

6. Relaxation Time and Penetration Depth

Relaxation time, τ is defined as the time taken by polar molecules to realign themselves to their original position when the electromagnetic field is removed. The τ is a characteristic of a material that is usually associated with the dipole reorientation time. The equation for relaxation time is given as,

$$\varepsilon'_r = -(\omega\varepsilon''_r)\tau + \varepsilon_s \tag{2}$$

where, ω is angular frequency ($\omega=2\pi f$), and ε_s is static permittivity when $\omega=0$. The relaxation time was determined from the slopes of ε' against $-\omega\varepsilon''$. Penetration depth, D_p is distance (in cm) inside the material at which the intensity has fallen to to $1/e$ (37%) of its incident value at the surface. The penetration depth is given as,

$$D_p = \frac{\lambda}{2\pi\varepsilon''_r}\sqrt{\varepsilon'_r} \tag{3}$$

where, λ (= c/f) is the operating wavelength and c (= 3×10^8 m/s) is the velocity of light in free space.

Table 2 shows the relaxation time, τ and penetration depth, D_p for some L- and S-series samples at microwave frequencies and different temperatures. The trend shows that τ decreases with increasing frequency. It can be said that the dipoles or molecules align themselves with the slowly alternating fields (at low frequency), thus resulting in the total polarization taking place in the material [16]. At high frequency, a stronger electromagnetic energy could interfere the polarization of the material and consequently decreasing the relaxation time [12]. Undeniably, the dielectric permittivity (ε'_r) decreases with the frequency due the finite relaxation time.

For char samples (S0.0 and S2.0), the relaxation time can be seen to be higher than the liquid samples (L0.0 and L1.0). The relaxation time of char may involve the whole molecule or a functional group anchored to a large molecule, and they depend on the intermolecular forces between the molecules and the size of the molecule [17]. Also, increasing the zinc chloride fraction in the solution (L1.0) increases the relaxation time.

Table 2. Temperature and Frequency Dependent of Relaxation Time and Penetration Depth

Sample	Frequency (GHz)	25°C		45°C	
		τ (ps)	D_p (cm)	τ (ps)	D_p (cm)
L0.0	0.915	5.62	13.6	17.2	17.8
	2.45	8.47	1.87	8.44	2.51
	5.8	8.38	0.345	6.85	0.461
L1.0	0.915	44.6	0.501	44.4	0.393
	2.45	14.8	0.401	10.3	0.346
	5.8	9.24	0.207	6.25	0.214
S0.0	0.915	202	121	31.6	158
	2.45	163	26.4	23.9	33.6
	5.8	149	11	128	11.2
S2.0	0.915	93.2	128	167	196
	2.45	45.8	29.1	56.1	32.2
	5.8	22.7	11	9.88	14.7

Penetration depth, D_p refers to the thickness of the material that microwave has to pass through in order for the material to be heated. Thus, higher D_p could be important for the material to be heated effectively via microwave. From Table 2, D_p for all materials slightly increased with increasing temperature.

Furthermore, D_p decreased with increasing frequency. It suggests that the microwave will only penetrate at the short distance and might only get absorbed just on the surface at higher frequency [16]. The penetration depth for electrolyte (L1.0) decreased because ionic conduction has larger influence on dielectric loss factor, ε''_r than the dielectric constant, ε'_r [11]. Again, appropriate selection of frequency is crucial in order to accommodate the differences in material composition and the phase change from suspension (solid-in-liquid) to solid for effective heating via microwave.

7. Conclusion

In microwave-assisted process of activated carbon production, the dielectric properties are dependent on frequency, composition and temperature. The presence of electrolyte improved the ability of the material to be heated using microwave. In addition, the penetration depth, D_p is dominant at lower frequency, and slightly increased with temperature. The material undergoes phase change and structural transformations, and so do the dielectric properties. The dielectric properties are specific only at a given frequency and state of the material. Hence, suitable operating frequency, preferably at 0.915 GHz would be appropriate for effective heating of zinc chloride-palm kernel shell mixture for the production of char and activated carbon.

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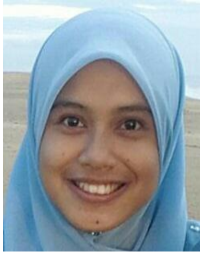

Nurul Zamani Mohammad Sabri was born in Kelantan in 1992. She was a research associate at the Centre of Lipids Engineering & Applied Research (CLEAR) and just graduated from Faculty of Chemical & Energy Engineering (FCEE), Universiti Teknologi Malaysia. Her work revolves around the measurement of dielectric properties and evaluation of adsorptive characteristics of zinc chloride treated palm kernel shell which earned her the B.Eng (Hons) in Chemical Engineering.

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