Diamond & Related Materials

Improved microwave absorption traits of coconut shells-derived activated carbon

--Manuscript Draft--

Manuscript Number:	DIAMOND-D-21-01052R1
Article Type:	Research Paper
Section/Category:	Other Carbons
Keywords:	Activated carbon; Milling; Fullerene-C70; Permeability; Permittivity; MW reflection loss
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Manuscript Region of Origin:	Asia Pacific
Abstract:	Novel multi-functional materials with very low microwave (MW) absorbance in the X-band became demanding for varied high-sensitive electronic applications. To meet this goal, a new type of activated carbon samples containing fullerene-C 70 was derived from coconut shells using the combined physical activation and milling process for the first time. The effects of various milling times (50, 75, and 100 minutes) on the structure, morphology, and MW reflection traits of these samples were examined. The crystalline phase of the activated fullerene-C 70 was found to alter from cubic to rhombohedral structure at the milling time of 100, displaying the specific surface area of 36525 m 2 /g and mean pore diameter of 3.42 nm. It was shown that by tuning the surface area and fullerene contents in the sample, the MW reflection loss of such activated carbon can be controlled. It is established that fullerene-C 70 derived from the proposed activated carbon may be useful to produce low-cost and efficient MW absorption materials needed for diverse electronic devices with reduced electromagnetic interference.
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Response to Reviewers:	

To
The Editor,
Diamond and Related Materials

Dear Sir / Madam,

We are pleased to submit our original manuscript entitled **"Improved microwave absorption traits of coconut shells-derived activated carbon"** authored by Wahyu Widanarto, Siska Irma Budianti, Sib Krishna Ghoshal, Candra Kurniawan, Erfan Handoko, Mudrik Alaydrus, for the peer-review and publication in **Diamond and Related Materials**.

We look forward to hearing from you at your earliest convenience.

Best regards,

Wahyu Widanarto

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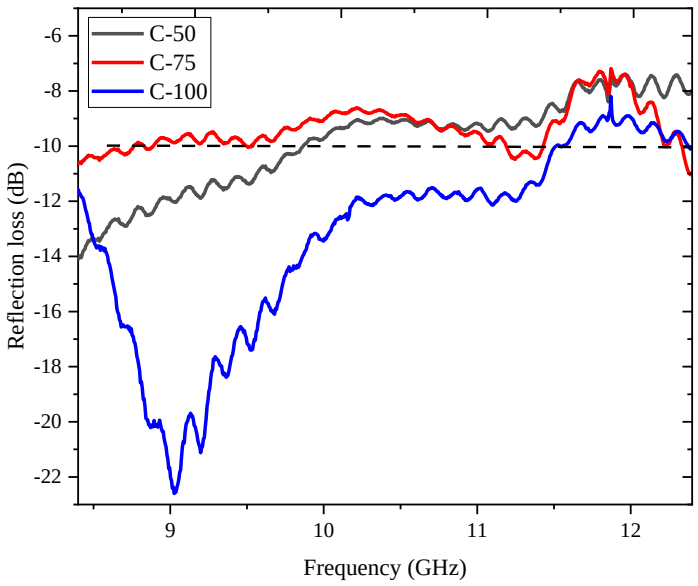
Graphical abstract



- Fullerene-C_{70} enriched activated carbon was derived from coconut shells via customized milling process.
- Prepared activated carbon showed high porosity and large specific surface area effective for MW X-band applications.
- Produced activated carbon revealed improved MW reflection loss due to the presence of fullerene-C_{70}.
- Structure, morphology and MW reflection loss loss of activated carbon were analyzed.
- Specific surface area, porosity and fullerene contents was shown to be tuned by increasing the milling times.

Declaration of Interest Statement for Diamond and Related Materials

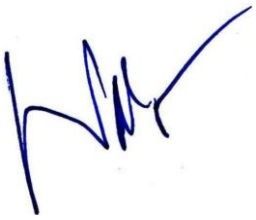
I, the Corresponding Author, declare that this manuscript entitled **Improved microwave absorption traits of coconut shells-derived activated carbon** is original, has not been published before and is not currently being considered for publication elsewhere.

I would like to draw the attention of the Editor to the following publications of one or more of us that refer to aspects of the manuscript presently being submitted.

I can confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. I further confirm that the order of authors listed in the manuscript has been approved by all of us.

I understand that the Corresponding Author is the sole contact for the Editorial process and is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

On behalf of the all-other authors
Corresponding Author,



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To
The Editor,
Diamond and Related Materials

Dear Sir / Madam,

We are pleased to submit our revised original manuscript entitled **"Improved microwave absorption traits of coconut shells-derived activated carbon"** authored by Wahyu Widanarto, Siska Irma Budianti, Sib Krishna Ghoshal, Candra Kurniawan, Erfan Handoko, Mudrik Alaydrus, for the peer-review and publication in **Diamond and Related Materials**.

We look forward to hearing from you at your earliest convenience.

Best regards,

Wahyu Widanarto

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The Editor

Diamond & Related Materials

MS. Ref No. DIAMOND-D-21-01052

Dear Sir,

Thanks to the reviewers for critical reading of the manuscript, providing invaluable comments and suggestions to modify it substantially. Please find attached herewith the responses to the reviewer's comments point by point on the revised manuscript (MS). The authors gratefully acknowledge the invaluable comments and advise by the reviewer. The reviewer comments are presented in *italics (BLACK)* and the corresponding replies as standard text in BLUE below each comment. The newly added texts are highlighted in YELLOW in the revised manuscript.

Reviewer's Comments:

Reviewer #1:

1) The specific surface area reported as 36525 m^2/g is highly doubtful.

Response: Thanks for your critical comment. Please note that we have recalculated the specific surface area and added some text with details of the method of calculation in the revised MS.

2) No explanation for effect of milling time on the respective values of permittivity values

Response: Thanks for the suggestions and very interesting question. Please note that it is very difficult to ascertain a correlation between milling time and permittivity values. However, we have well taken your advice for our future studies.

3) There is no scientific explanation regarding the variation of BET data for different samples.

Response: Thanks for your critical observation and comments. Please note that we have added the scientific explanation in the revised MS.

4) No confirmation for fullerene C70

Response: Thanks for your critical observation and comments. Please note that the existence of fullerene C70 is confirmed by XRD data.

Reviewer #2:

The manuscript proposes a new type of activated carbon samples containing fullerene-C70 with great microwave absorbing in the X band. The MW reflection loss of such activated carbon can be controlled by tuning the increase of milling time. Fullerene-C70 derived from the proposed activated carbon may be useful to produce low-cost and efficient MW absorption materials needed

for diverse electronic devices with reduced electromagnetic interference. I think it is appropriate for this paper to be accepted by Diamond & Related Materials, as long as the following comments are answered.

1. According to authors, the microwave absorbing material prepared in the manuscript are innovative. Please compare with the relevant research results in the past three years and list some novelties.

Response: Thanks for your critical observation, sincere comments, and invaluable advice. We admire your question and will follow the advice in our next publication in the same journal which is underway. Please note that we have searched for the relevant literatures on this material over last three years for a comparative evaluation. However, we failed to find any data on activated carbon materials prepared by this method for comparison.

To the best of our knowledge the proposed product is totally new and our systematic approach to achieve improved MW absorption for X-band applications is innovative. Furthermore, for sustainable development, at present, low cost natural materials and methods following the green chemistry route are very much required. The present effort is just an attempt to accomplish bigger goal in the future.

2. Authors mention "In addition, the permeability and permittivity of such activated carbon were improved with the increase of milling time"(in abstract). But figure 5 shows the ε', ε'', μ' and μ'' of activated carbon do not always have the same change trend with the increase of milling time in different frequence.

Response: Thanks for your useful comments and observation. We totally agree with the comments and please note that we have deleted the statement from the abstract in the revised MS.

3. Authors mention "Activated carbon obtained as milling time of 100 minutes was the optimum one in terms of structures, morphology", C-70 and C-100 also need SEM images to explain the effects of various milling times (50, 75, and 100 minutes) on the structure, morphology of C70.

Response: Thanks for your valuable advice. Please note that we have added the SEM images of C-50,75 and 100 in the revised MS for better explanation.

4. In figure5, μ' of C-100 has an oscillation in the high frequency region. Please explain why it appears.

Response: Thanks for your valuable question. Please note that the permeability being the magnetic property of a material, generally a natural resonance occurs when an external electromagnetic radiation is applied to the magnetic material. In this view, the relationship between the resonant frequency f_r and the anisotropic field (H_A) can be expressed as:

$$2\pi f_r = \gamma H_A$$

where γ is the absolute gyromagnetic ratio. Essentially, a strong anisotropic field can cause a very high resonance frequency as observed.

Improved microwave absorption traits of coconut shells-derived activated carbon

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ABSTRACT

Novel multi-functional materials with very low microwave (MW) absorbance in the X-band became demanding for varied high-sensitive electronic applications. To meet this goal, a new type of activated carbon samples containing fullerene-C_{70} was derived from coconut shells using the combined physical activation and milling process for the first time. The effects of various milling times (50, 75, and 100 minutes) on the structure, morphology, and MW reflection traits of these samples were examined. The crystalline phase of the activated fullerene-C_{70} was found to alter from cubic to rhombohedral structure at the milling time of 100, displaying the specific surface area of 36525 m^2/g and mean pore diameter of 3.42 nm. It was shown that by tuning the surface area and fullerene contents in the sample, the MW reflection loss of such activated carbon can be controlled. It is established that fullerene-C_{70} derived from the proposed activated carbon may be useful to produce low-cost and efficient MW absorption materials needed for diverse electronic devices with reduced electromagnetic interference.

Keywords: Activated carbon, Milling, Fullerene-C_{70}, Permeability, Permittivity, MW reflection loss

1. Introduction

With the development of microwave (MW)-based electronic technology electromagnetic wave pollution became a serious environmental concern, greatly affecting human health and normal operations of electronic devices. To mitigate these problems, electromagnetic wave absorbing materials have intensively been researched in recent years. Coating the target with an efficient electromagnetic wave absorbing material is a method to reduce the intensity of the reflected or transmitted electromagnetic waves [1–7]. This method utilizes the absorption or dispersion of electromagnetic energy in the medium between the electromagnetic wave source and the protected target. It imparts the electromagnetic wave absorbing materials the ability to absorb unwanted electromagnetic waves and stability against temperature and oxidation. In addition, they are easy to manufacture, flexible and affordable to become one of the *high-tech* essential materials.

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Extensive research revealed that the performance of the carbon nanomaterials and their composites like graphene, carbon spheres, carbon nanotubes are great potential in attenuating the electromagnetic waves [8–12]. Activated carbon is a carbon source that can be obtained by activating carbon physically or chemically. The surface morphology of the porous activated carbon is one of the unique characteristics that can be used in many applications such as dye absorbers, oil purification, supercapacitor electrodes, secondary battery electrodes, and others [8,13–16]. Some recent studies revealed that porous carbon nanostructures are advantageous to enhance their electromagnetic wave absorption characteristics [17,18]. Essentially, the magnetic components insertion inside the carbon materials [19,20] and hollow carbon spheres [21,22] are the effective strategies to appreciably improve the electromagnetic radiation absorption performance of the resultant products. However, to revalidate such claims more systematic investigations on new types of activated carbon nanomaterials are needed.

Considering the immense applied potential of the activated carbon materials, some activated carbon was derived from the coconut shell using the milling technique to achieve their improved MW absorption properties in the X-band. The milling times were varied to modify the structures, morphologies and electromagnetic radiation absorption attributes of the proposed activated carbon enclosing fullerene-C_{70}. A porous surface of the activated carbon with a very small volume was used to warp electromagnetic waves so that the internal surface reflections in the volume occurred, thus improving the heat dissipation quality of the electromagnetic energy. The as-prepared activated carbon samples were characterized to determine their milling time-dependent surface morphology, structure, specific surface area, porosity, and MW absorbance (in terms of reflection loss values) in the X-band.

2. Experimental

2.1. Preparation of activated carbon from coconut shells

Carbon was made via the carbonization process wherein coconut shells were burnt at 80°C for an hour under oxygen-deficient conditions to eliminate the organic materials present in the shells. The loss of organic materials triggered the formation or opening of the carbon pores. Then, the burnt coconut shell-derived carbon was physically activated. Intense heat and water vapor enabled the severing of the carbon chains from the organic compounds. The heating as the physical activation process was intended to remove the impurities and impure hydrocarbons from the

activated carbon. Next, the resultant carbon was heated in the temperature range of 800-900°C followed by the water vapor streaming. The water vapor reacted with carbon, thus releasing carbon monoxide, carbon dioxide, and hydrogen. Thereafter, the activated carbon was pulverized using a Mill Shaker at different milling times of 50, 75, and 100 minutes to obtain the particles' sizes in the micrometer range. The extracted activated carbon powders were labeled as C-50, C-75, and C-100 according to various milling times. A small amount of activated carbon was bound utilizing resin to form a rectangular shape steady with the WR90 sample holder for measuring the reflection loss (R_L).

2.2. Characterizations

The morphology and microstructure of the prepared samples (C-50, C-75, and C-100) were examined using the field emission scanning electron microscope (FESEM JIB-4610F). The crystal structures and phases of the samples were measured using a SmartLab (3 kW) X-ray diffractometer equipped with the Cu–Kα line of wavelength (λ) ≈ 0.1541874 nm. The Surface Area Analyzer (SAA Quantachrome Instrument Version 11.03) was used to determine the specific surface area and pore diameter of the samples. The scattering characteristics (S) of the specimens were measured using a vector network analyzer (VNA) from Keysight (PNA-L N5232A). The MW absorbance values of the samples were calculated to get the components of S (S_{11}, S_{12}, S_{21}, and S_{22}). The values of S_{11} and S_{21} specify the coefficients of reflection (Γ) and transmission (T), respectively. The recorded values of S_{22} and S_{12} were ignored due to their corresponding similarity with S_{11} and S_{21}. The values of complex relative permeability (μ_r) and permittivity (ε_r) were calculated using the Nicholson-Ross-Weir (NRW) method. In addition, the transmission/reflection line concept was used to calculate the reflection loss (R_L) of the samples, yielding the MW absorption characteristics.

3. Results and Discussion

3.1. Morphology of the activated carbon

Fig. 1 shows the SEM micrographs of the activated carbons that are pulverized at different milling times, which consisted of irregular microstructures. Interestingly, the formation of carbon particles with inter-granular pores provided a large specific surface area that is suitable for strong interaction with the externally applied electromagnetic radiation. Together, these pores strongly

favored the MW entrapment and its random dispersion in all directions facilitated by the finer particles in the pores, thereby improving the MW absorption traits of the proposed activated carbon specimen. In addition, several smaller particles were merged to form bigger particles through surface free energy minimization, indicating their thermodynamic stable state. Indeed, the growth and nucleation became more prominent in the C-100 specimen, leading to a significant difference in its reflectivity.

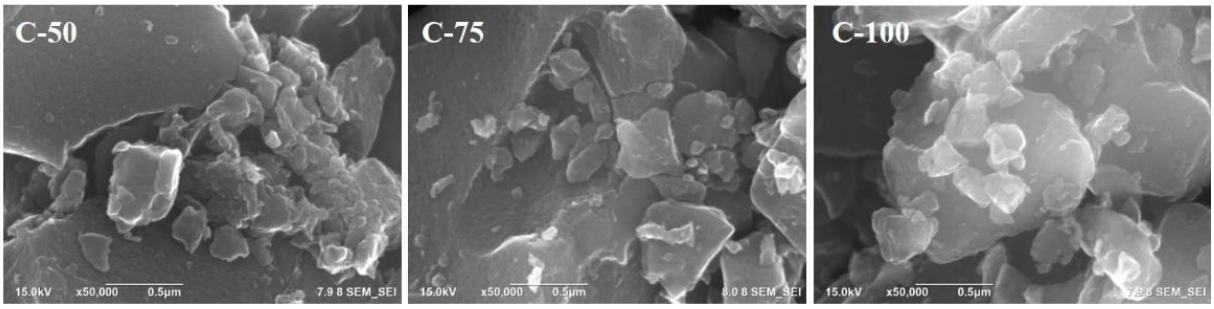

Fig. 1. Morphology of the activated carbon which is milled at different milling time

3.2. Structures and phase of the activated carbon

Fig. 2 displays the X-ray diffraction (XRD) patterns of all the milled samples. The XRD peaks of C-50 sample were matched to the cubic carbon (C – ICDD: 00-006-0675) with crystallographic parameters of $a = b = c = 0.35667$ nm and $\alpha = \beta = \gamma = 90°$. Similar observations were made for C-75 and C-100 samples wherein the Bragg's peaks were dominated by the cubic carbon lattice (C – ICDD: 00-006-0675). Sample grown at the milling times of 100 minutes (C-100) consisted of fullerene-C_{70} carbon phase (C- ICDD 00-048-1449), showing intense XRD peak at $2\theta = 23.90°$ with crystallographic parameters of $a = b = 0.98095$ nm, $c = 2.70220$ nm, and $\alpha=\beta= 90°$, $\gamma=120°$. It is known that fullerene-C_{70} enclosing seventy carbon atoms has a spherical caged structure made of 25 hexagons and 12 pentagons connected by single and double covalent bonds. Due to this unique structure of fullerenes, strong internal reflections occur in the spherical cage, thus enabling it a gifted MW absorber. Earlier studies indicated that fullerene being one of the efficient reinforcing materials can be greatly effective in absorbing MW radiation[23]. In addition, it was claimed that the graphite – fullerene composites can exhibit excellent MW absorption performance compared to pure graphite [24] which needs further validation.

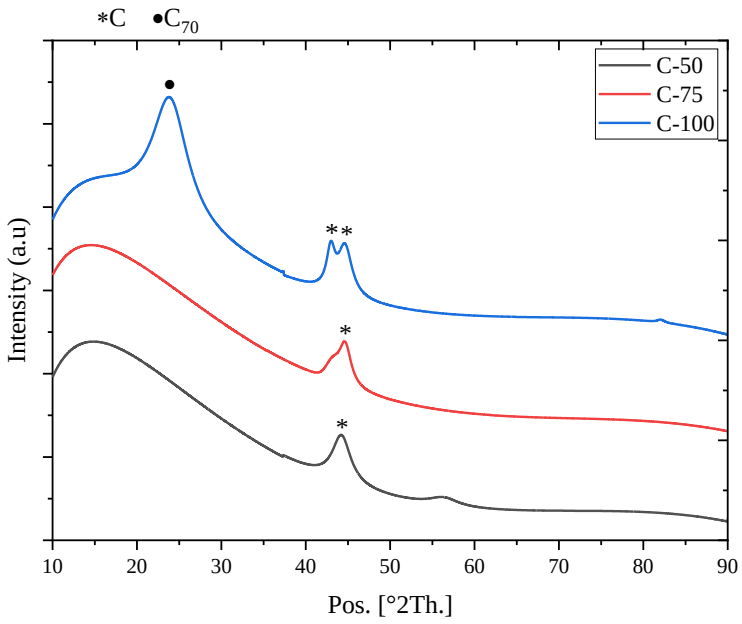

Fig. 2. XRD patterns of the as-prepared C-50, C-75, and C-100 samples with indicated carbon phases of ∗ C and ● C_{70}

3.3. *Specific surface area and pore diameter of the activated carbon*

Fig. 3 illustrates a multi-point isothermal BET plot of the activated carbon samples. Brunauer, Emmett, and Teller (BET) methods were applied to evaluate the specific surface area (m^2/g) of the samples (Table 1). These specific surface areas were used to determine the diffusion process through the porous material and selectivity for the catalyst reaction explained using the adsorption theory. The BET equation was used on the adsorption isotherms with P/P_0 values ranging from 0.05-0.3. The isothermal BET equation can be written as:

$$\frac{1}{W\left(\frac{P_0}{P}\right)-1} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C}\right]\frac{P}{P_0} \quad (1)$$

where W denotes the volume of absorbed gas at the relative pressure P/P_0, V_m is the volume of nitrogen gas that formed a monolayer at a solid surface, P is the pressure of adsorption equilibrium, P_0 is the pressure of adsorption saturation and C is the constant of energy.

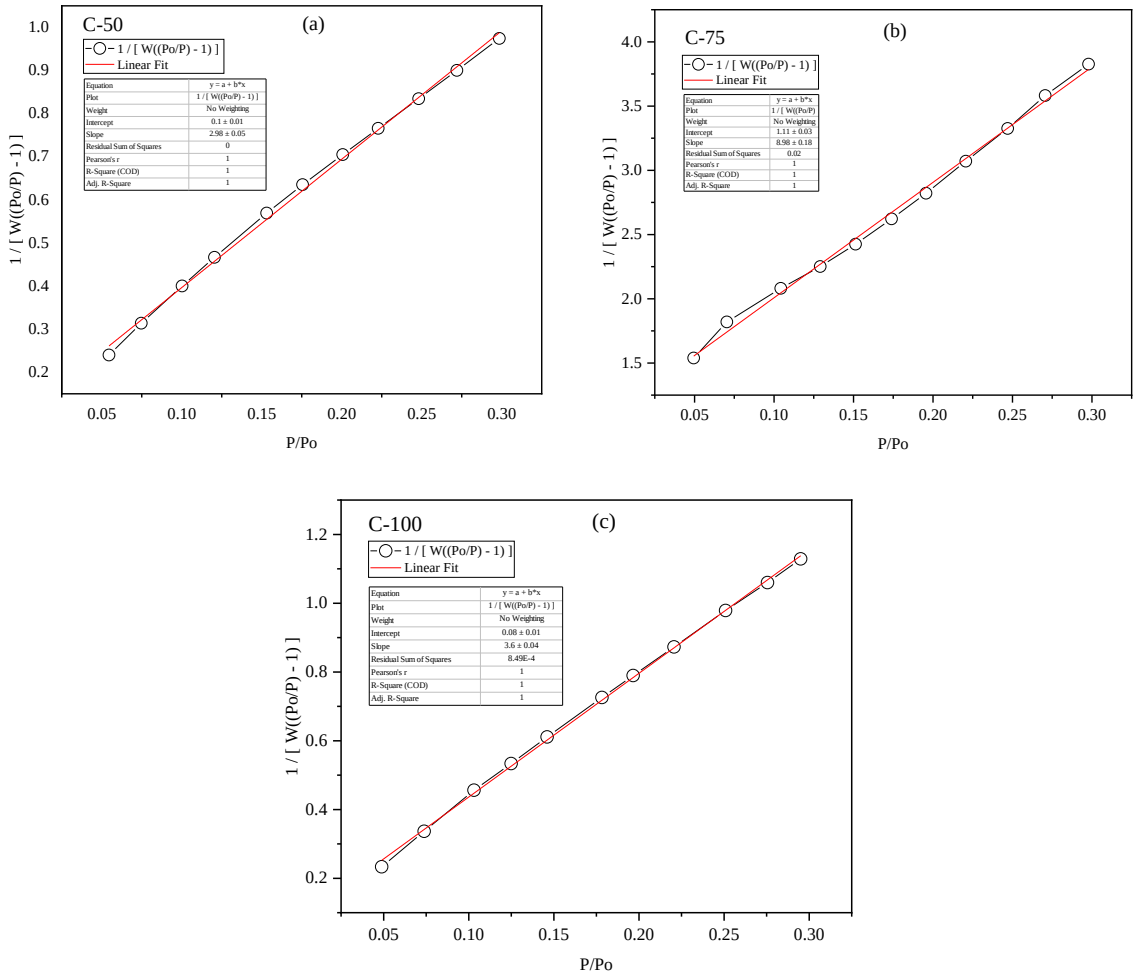

Fig. 3. Multi-point isothermal BET plot of all activated carbon specimens

The values of V_m for all the samples were estimated from the slope (s) and intercepts (i) on the BET chart, achieving the total and specific surface areas of the produced activated carbon given by:

$$s = \frac{C-1}{V_m C} \quad (2)$$

$$i = \frac{1}{V_m C} \quad (3)$$

Combining Eq. 1 and 2, one obtains:

$$V_m = \frac{1}{s+i} \quad (4)$$

The BET method was used to calculate the surface area of the sample which can be defined as the number of pores in each unit area of the sample. The expression for total surface area (S_t) can be written as:

$$S_t = \frac{V_m N A_{cs}}{M} \quad (5)$$

where N is the Avogadro's number (6.023×10^{23} mol^{-1}), A_{cs} is the cross-section area (10.2 Å) and M is the molecular weight (28.013 g/mol) of nitrogen.

The specific surface area (S) calculated from the ratio of total surface area to the mass (m) of the solid sample or adsorbent can be written as [25]:

$$S = \frac{S_t}{m} \quad (6)$$

Table 1. The total surface area and specific surface area of the activated carbons

Sample Code	Total surface area (m^2)	Specific surface area (m^2/g)
C-50	1130	50266
C-75	345	13000
C-100	947	36525

Fig. 4 depicts the Barret Joyner Hallenda (BJH) pore size distribution - nitrogen adsorption at 77.35 K for C-50, C-75, and C-100 samples. Irrespective of the milling times, the pore radius distribution of the samples was in the range of 1 and 250 nm wherein the maximum peaks occurred at 1.53 (for C-50), 1.94 (for C-75), and 1.71 nm (for C-100). The average pore diameters of C-50, C-75, and C-100 samples were 3.06, 3.88, and 3.42 nm, respectively. According to the International Union of Pure Applied Chemistry (IUPAC) standard, the resulting pore diameters were classified as mesopores (pore diameter range of 2-50 nm). In addition, the pore volumes of C-50, C-75, and C-100 samples were 1.02×10^{-6}, 6×10^{-8}, and 7.4×10^{-7} m^3/g, respectively.

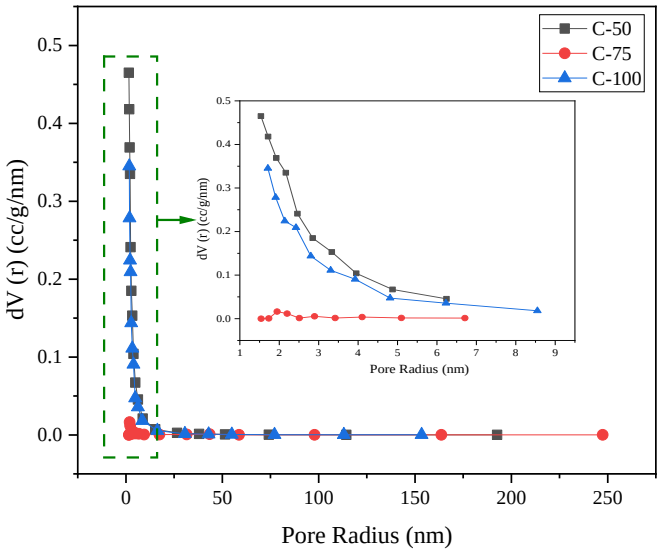

Fig. 4. BJH pore size distribution – nitrogen adsorption at 77.35 K for all activated carbon samples

Figs. 3 and 4 clearly revealed the activated carbon samples have a large specific surface area and excellent porosity. This porous morphology plays a significant role in the MW absorption, where a decrease in the pore diameter can appreciably increase the material's density or cavity concentration, thus leading to an alteration in the specific surface area responsible for the MW absorption. Consequently, an improvement in the specific surface area and porosity of the samples enables more interaction between carbon atoms and MW on the surfaces and interfaces.

2.3. Complex relative permeability and permittivity of the activated carbon

Fig. 5 displays the complex relative permeability and permittivity of C-50, C-75, and C-100 samples measured in the frequency range of 8.2-12.4 GHz. It is worth noting that the real permeability values of C-50, C-75, and C-100 samples were comparable due to their almost similar crystal phases. Conversely, the C-100 sample showed higher magnetic energy storage capacity (higher value of real permeability) than the C-50 and C-75 samples. Irrespective of the milling times, the real permeability values for all samples were gradually decreased to zero with the increase of MW frequency (Fig. 5(a)). The imaginary permeability of the C-100 sample (Fig. 5(b)) was related to magnetic loss which dropped significantly to almost zero in the range of 8.2 to 9

GHz and then fluctuated near zero. Meanwhile, the real permittivity of C-50 and C-75 samples (Fig. 5(c)) exhibited gradual declination trends with the increase of frequency. However, the real permittivity of the C-100 sample remained steady with the increase of frequency, indicating an excellent electrical field energy storage performance of C-100. The real permittivity (or dielectric constant) also determines how much the incoming energy can be reflected and absorbed by the proposed activated carbon. In the frequency range of 8.2 and 9.3 GHz, the imaginary permittivity (or dielectric loss factor) of C-100 was considerably increased (Fig. 5(d)) that assessed the dissipation of electrical field energy in the form of heat inside the activated carbon.

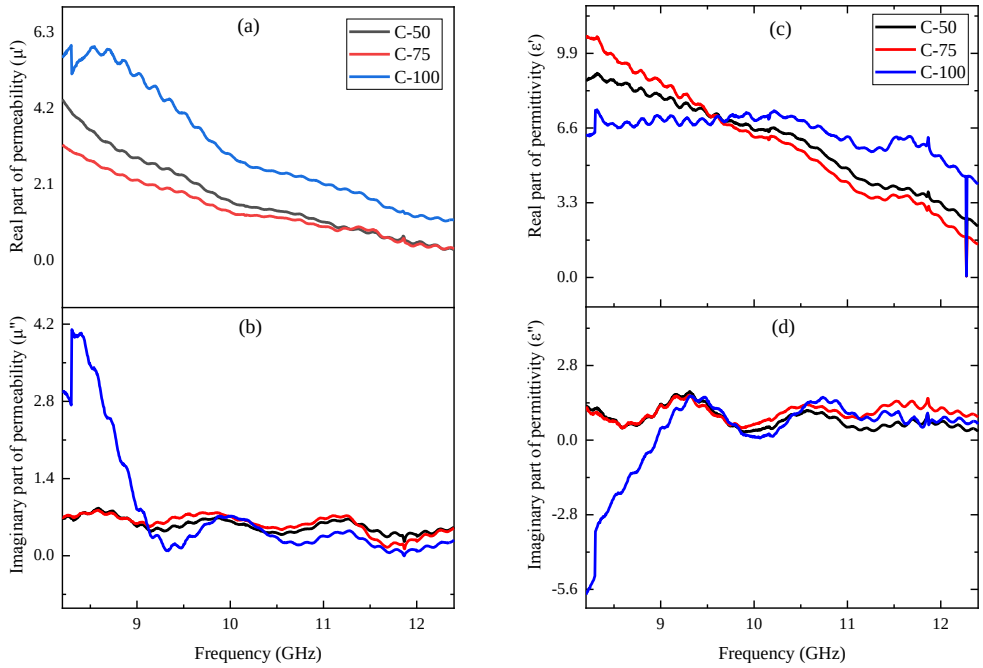

Fig. 5. MV frequency-dependent complex relative permeability and permittivity of 4 mm thick activated carbon.

2.4. Microwave reflection loss of activated carbon

Fig. 6 illustrates the MW absorption properties of all activated carbon specimens in terms of their frequency-dependent reflection loss (R_L). The R_L was found to be controlled by adjusting the milling time. The patterns of R_L for C-50 and C-75 were similar with an average value of approximately -10 dB. Conversely, the C-100 sample exhibited a prominent absorption band around 9 GHz with a bandwidth of 3 GHz. Interestingly, mesoporous C-100 sample containing

fullerene-C_{70} revealed significant MW absorbance in the X-band, indicating its potential as MW X-band applications in electronic devices. The produced fullerene-C_{70} dominated activated carbon also showed outstanding permeability and permittivity, suggesting its appropriateness for the MW X-band applications. Furthermore, the occurrence of a weak oscillation in the high-frequency range was attributed to the internal surface reflection within the mesopores. It was asserted that the milling process with optimal milling time could substantially enhance the microwave absorption capacity of the activated carbon. In short, the suggested fullerene-C70 enclosed activated carbon can lead to the development of low-cost, high-efficiency MW absorption materials desired for sundry applications.

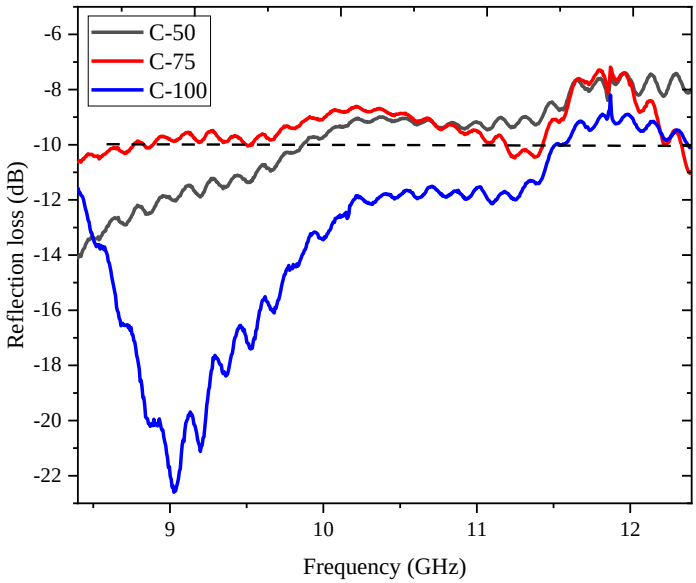

Fig. 6. MW reflection loss as a function of frequency for all activated carbon specimens

4. Conclusions

For the first time novel activated carbon specimens (C-50, C-75, and C-100) were prepared from the coconut shells using a modified milling process plus heating process. The milling times were varied (50, 75, and 100 minutes) to get mesoporous activated carbon with improved MW absorption properties. The surface morphology, phase, structure, surface area, porosity, and MW reflection loss of these samples were improved with the increase of milling times. Activated carbon obtained as milling time of 100 minutes was the optimum one in terms of structures, morphology,

and MW absorbance. The C-100 sample showed a phase transformation from cubic to the rhombohedral crystal structure (or fullerene-C_{70}). The surface area and mean pore diameter of the C-100 specimen were 36525 m^2/g and 3.42 nm, respectively. The activated carbon-containing fullerene-C_{70} revealed excellent permeability and permittivity characteristics suitable for MW X-band applications. It was affirmed that by regulating the surface area and fullerene-C_{70} contents in the activated carbon the MW reflection loss can be tuned. The proposed fullerene-C_{70} based activated carbon can lead to the development of cheap and efficient MW absorption materials required for varied purposes.

Acknowledgments

The authors are grateful to the Universitas Jenderal Soedirman (Contract number: T/573/UN.23.18/PT.01.03/2021) and UTM Malaysia (UTMFR 20H65) for their financial assistance.

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Diamond & Related Materials

Improved microwave absorption traits of coconut shells-derived activated carbon

--Manuscript Draft--

Manuscript Number:	DIAMOND-D-21-01052R2
Article Type:	Research Paper
Section/Category:	Other Carbons
Keywords:	Activated carbon; Milling; Fullerene-C70; Permeability; Permittivity; MW reflection loss
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Manuscript Region of Origin:	Asia Pacific
Abstract:	Novel multi-functional materials with very high microwave (MW) absorbance in the X-band became demanding for varied high-sensitive electronic applications. To meet this goal, a new type of activated carbon sample containing fullerene-C70 was derived from coconut shells using the combined physical activation and milling process for the first time. The effects of various milling times (50, 75, and 100 minutes) on the structure, morphology, and MW reflection traits of these samples were examined. The crystalline phase of the activated fullerene-C70 was found to alter from cubic to rhombohedral structure at the milling time of 100, displaying a specific surface area of 946.499 m2/g and mean pore diameter of 3.42 nm. It was shown that by tuning the surface area and fullerene contents in the sample, the MW reflection loss of such activated carbon can be controlled. It is established that fullerene-C70 derived from the proposed activated carbon may be useful to produce low-cost and efficient MW absorption materials needed for diverse electronic devices with reduced electromagnetic interference.
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Response to Reviewers:	

To
The Editor,
Diamond and Related Materials

Dear Sir / Madam,

We are pleased to submit our original manuscript entitled **"Improved microwave absorption traits of coconut shells-derived activated carbon"** authored by Wahyu Widanarto, Siska Irma Budianti, Sib Krishna Ghoshal, Candra Kurniawan, Erfan Handoko, Mudrik Alaydrus, for the peer-review and publication in **Diamond and Related Materials**.

We look forward to hearing from you at your earliest convenience.

Best regards,

Wahyu Widanarto

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The Editor

Diamond & Related Materials

MS. Ref No. DIAMOND-D-21-01052

Dear Sir,

Thanks to the reviewers for critical reading of the manuscript, providing invaluable comments and suggestions to modify it substantially. Please find attached herewith the responses to the reviewer's comments point by point on the revised manuscript (MS). The authors gratefully acknowledge the invaluable comments and advise by the reviewer. The reviewer comments are presented in *italics (BLACK)* and the corresponding replies as standard text in BLUE below each comment. The newly added texts are highlighted in YELLOW in the revised manuscript.

Reviewer's Comments:

Reviewer #1:

The reported Specific surface area is not admissible... As well as other explanation is not satisfactorily explained, so i feel that the paper is not acceptable in this reputed journal.

Reviewer #2:

All issues have been addressed adequately and the manuscript can be published in the current form.

Reviewer #3:

The manuscript discussed a type of activated carbon from coconut shells for microwave absorption in the X-band. The microwave absorption of the products can be tuned through the milling time. There are some points need the author to clarify.

1. The graphical abstract is suggested to be improved to make it more meaningful.

Graphical abstract has been improved

2. In the Abstract, what does it mean by "with very low microwave absorbance"?

Thanks for the critical observation. Please note that we have corrected it in the revised manuscript.

3. The reflection loss of the product is calculated in this work.

Thanks for the useful comment. Please note that we have added the detail calculation procedure of the reflection in the revised manuscript

4. The specific surface area values of the products in Table 1 are not correct. Activated carbon with such a large size in Figure 1 cannot have so big a specific surface area.

Thanks for the careful observation and pointing out the mistakes. Please note that we have recalculated the specific surface area (S_{BET}) and added them together with the details of the calculation procedure in the revised manuscript.

5. There is definitely some problem with the electromagnetic parameters testing as listed in Figure 5. Especially, there is no reason that the activated carbon exhibits negative imaginary permittivity values in the X-band frequency range. It is highly recommended to check the calibration carefully.

Thanks for the useful comment and critical observation. Please note that we have checked the calibration and testing procedure carefully to see if there are any errors with the measurement. However, we could not find any flaw. To the best of our knowledge, the material media that exhibit energy loss for the signal show positive imaginary permittivity. However, the material media having energy gain from the interacting electromagnetic signal display negative imaginary permittivity. Usually, some metamaterials with negative refractive indices show such behavior. In the present case, the emergence of negative imaginary permittivity values may be due the different crystal structure similar to metamaterials. This is only possible reason that we can provide at the moment. More careful and precise investigation may unfold such interesting results.

6. The fluctuations in the RL curves in Figure 6 are mainly caused by the incorrectly measured parameters. Also, RL is thickness dependent, so the author should give the thickness for the RL calculation.

Thanks for the careful observation and advises. Please note that we have included the sample thickness (4 mm) in the calculation of R_L. In addition, we agree with your comment and it may be due to the impreciseness in the measured parameters that require further studies. However, the fluctuation is quite systematic and much tinier compared to the average values.

Declaration of Interest Statement for Diamond and Related Materials

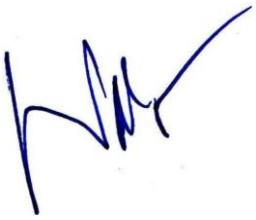
I, the Corresponding Author, declare that this manuscript entitled **Improved microwave absorption traits of coconut shells-derived activated carbon** is original, has not been published before and is not currently being considered for publication elsewhere.

I would like to draw the attention of the Editor to the following publications of one or more of us that refer to aspects of the manuscript presently being submitted.

I can confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. I further confirm that the order of authors listed in the manuscript has been approved by all of us.

I understand that the Corresponding Author is the sole contact for the Editorial process and is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

On behalf of the all-other authors
Corresponding Author,



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To
The Editor,
Diamond and Related Materials

Dear Sir / Madam,

We are pleased to submit our revised original manuscript entitled **"Improved microwave absorption traits of coconut shells-derived activated carbon"** authored by Wahyu Widanarto, Siska Irma Budianti, Sib Krishna Ghoshal, Candra Kurniawan, Erfan Handoko, Mudrik Alaydrus, for the peer-review and publication in **Diamond and Related Materials**.

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Improved microwave absorption traits of coconut shells-derived activated carbon

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ABSTRACT

Novel multi-functional materials with very high microwave (MW) absorbance in the X-band became demanding for varied high-sensitive electronic applications. To meet this goal, a new type of activated carbon sample containing fullerene-C_{70} was derived from coconut shells using the combined physical activation and milling process for the first time. The effects of various milling times (50, 75, and 100 minutes) on the structure, morphology, and MW reflection traits of these samples were examined. The crystalline phase of the activated fullerene-C_{70} was found to alter from cubic to rhombohedral structure at the milling time of 100, displaying a specific surface area of 946.499 m^2/g and mean pore diameter of 3.42 nm. It was shown that by tuning the surface area and fullerene contents in the sample, the MW reflection loss of such activated carbon can be controlled. It is established that fullerene-C_{70} derived from the proposed activated carbon may be useful to produce low-cost and efficient MW absorption materials needed for diverse electronic devices with reduced electromagnetic interference.

Keywords: Activated carbon, Milling, Fullerene-C_{70}, Permeability, Permittivity, MW reflection loss

1. Introduction

With the development of microwave (MW)-based electronic technology electromagnetic wave pollution became a serious environmental concern, greatly affecting human health and normal operations of electronic devices. To mitigate these problems, electromagnetic wave absorbing materials have intensively been researched in recent years. Coating the target with an efficient electromagnetic wave absorbing material is a method to reduce the intensity of the reflected or transmitted electromagnetic waves [1–7]. This method utilizes the absorption or dispersion of electromagnetic energy in the medium between the electromagnetic wave source and the protected target. It imparts the electromagnetic wave absorbing materials the ability to absorb unwanted electromagnetic waves and stability against temperature and oxidation. In addition, they are easy to manufacture, flexible and affordable to become one of the *high-tech* essential materials.

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Extensive research revealed that the performance of the carbon nanomaterials and their composites like graphene, carbon spheres, carbon nanotubes are great potential in attenuating the electromagnetic waves [8–12]. Activated carbon is a carbon source that can be obtained by activating carbon physically or chemically. The surface morphology of the porous activated carbon is one of the unique characteristics that can be used in many applications such as dye absorbers, oil purification, supercapacitor electrodes, secondary battery electrodes, and others [8,13–16]. Some recent studies revealed that porous carbon nanostructures are advantageous to enhance their electromagnetic wave absorption characteristics [17,18]. Essentially, the magnetic components insertion inside the carbon materials [19,20] and hollow carbon spheres [21,22] are the effective strategies to appreciably improve the electromagnetic radiation absorption performance of the resultant products. However, to revalidate such claims more systematic investigations on new types of activated carbon nanomaterials are needed.

Considering the immense applied potential of the activated carbon materials, some activated carbon was derived from the coconut shell using the milling technique to achieve their improved MW absorption properties in the X-band. The milling times were varied to modify the structures, morphologies, and electromagnetic radiation absorption attributes of the proposed activated carbon enclosing fullerene-C_{70}. A porous surface of the activated carbon with a very small volume was used to warp electromagnetic waves so that the internal surface reflections in the volume occurred, thus improving the heat dissipation quality of the electromagnetic energy. The as-prepared activated carbon samples were characterized to determine their milling time-dependent surface morphology, structure, specific surface area, porosity, and MW absorbance (in terms of reflection loss values) in the X-band.

2. Experimental

2.1. Preparation of activated carbon from coconut shells

Carbon was made via the carbonization process wherein coconut shells were burnt at 80°C for an hour under oxygen-deficient conditions to eliminate the organic materials present in the shells. The loss of organic materials triggered the formation or opening of the carbon pores. Then, the burnt coconut shell-derived carbon was physically activated. Intense heat and water vapor enabled the severing of the carbon chains from the organic compounds. The heating as the physical activation process was intended to remove the impurities and impure hydrocarbons from

the activated carbon. Next, the resultant carbon was heated in the temperature range of 800-900°C followed by the water vapor streaming. The water vapor reacted with carbon, thus releasing carbon monoxide, carbon dioxide, and hydrogen. Thereafter, the activated carbon was pulverized using a Mill Shaker at different milling times of 50, 75, and 100 minutes to obtain the particles' sizes in the micrometer range. The extracted activated carbon powders were labeled as C-50, C-75, and C-100 according to various milling times. A small amount of activated carbon was bound utilizing resin to form a rectangular shape steady with the WR90 sample holder for measuring the reflection loss (R_L).

2.2. Characterizations

The morphology and microstructure of the prepared samples (C-50, C-75, and C-100) were examined using the field emission scanning electron microscope (FESEM JIB-4610F). The crystal structures and phases of the samples were measured using a SmartLab (3 kW) X-ray diffractometer equipped with the Cu–Kα line of wavelength (λ) ≈ 0.1541874 nm. The Surface Area Analyzer (SAA Quantachrome Instrument Version 11.03) was used to determine the specific surface area and pore diameter of the samples. The scattering characteristics (S) of the specimens were measured using a vector network analyzer (VNA) from Keysight (PNA-L N5232A). The MW absorbance values of the samples were calculated to get the components of S (S_{11}, S_{12}, S_{21}, and S_{22}). The values of S_{11} and S_{21} specify the coefficients of reflection (Γ) and transmission (T), respectively. The recorded values of S_{22} and S_{12} were ignored due to their corresponding similarity with S_{11} and S_{21}. Following the method of Nicholson-Ross-Weir (NRW), the relative complex permeability ($\mu_r = \mu' - j\mu''$) and permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) values of 4 mm thick samples were calculated using:

$$\mu_r = \frac{1+\Gamma}{\Lambda(1-\Gamma)\sqrt{\frac{1}{\lambda_0^2}-\frac{1}{\lambda_c^2}}} \quad (1)$$

$$\frac{1}{\Lambda^2} = -\left[\frac{1}{2\pi d} ln\left(\frac{1}{T}\right)\right]^2 \quad (2)$$

$$\varepsilon_r = \frac{\lambda_0^2}{\mu_r}\left(\frac{1}{\lambda_c^2} - \left[\frac{1}{2\pi d} ln\left(\frac{1}{T}\right)\right]^2\right) \quad (3)$$

where λ_0 is the wavelength in vacuum, λ_c is the cut-off wavelength, c is the speed of light, and d is the thickness of the sample. Meanwhile, the MW absorption properties of the samples were obtained from the calculated reflection loss (R_L) values based on the transmission/reflection line theory [7,23–26] given by:

$$R_L = 20\,log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (4)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\,tan\left[-j\frac{2\pi f d}{c}\sqrt{\mu_r \varepsilon_r}\right] \quad (5)$$

where Z_{in} is the input impedance of the material and f is the MW frequency.

3. Results and Discussion

3.1. Morphology of the activated carbon

Fig. 1 shows the SEM micrographs of the activated carbons that are pulverized at different milling times, which consisted of irregular microstructures. Interestingly, the formation of carbon particles with inter-granular pores provided a large specific surface area that is suitable for strong interaction with the externally applied electromagnetic radiation. Together, these pores strongly favored the MW entrapment and its random dispersion in all directions facilitated by the finer particles in the pores, thereby improving the MW absorption traits of the proposed activated carbon specimen. In addition, several smaller particles were merged to form bigger particles through surface free energy minimization, indicating their thermodynamic stable state. Indeed, the growth and nucleation became more prominent in the C-100 specimen, leading to a significant difference in its reflectivity.

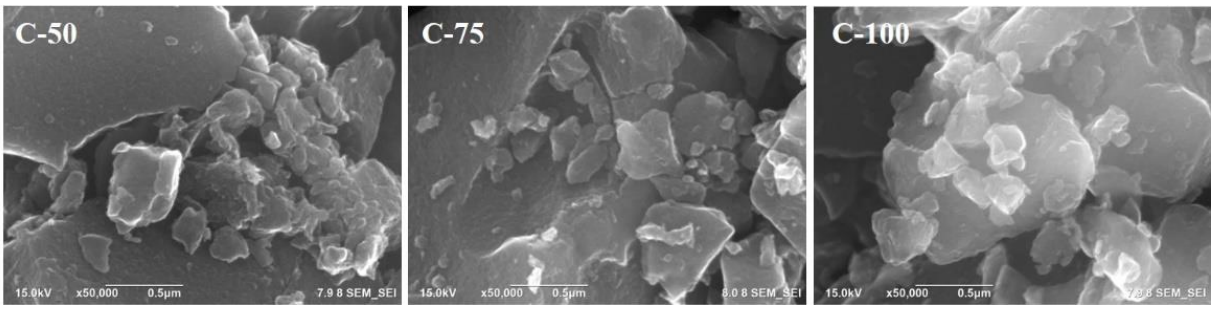

Fig. 1. Morphology of the activated carbon which is milled at different milling time

3.2. *Structures and phase of the activated carbon*

Fig. 2 displays the X-ray diffraction (XRD) patterns of all the milled samples. The XRD peaks of C-50 sample were matched to the cubic carbon (C – ICDD: 00-006-0675) with crystallographic parameters of $a = b = c = 0.35667$ nm and $\alpha = \beta = \gamma = 90°$. Similar observations were made for C-75 and C-100 samples wherein the Bragg's peaks were dominated by the cubic carbon lattice (C – ICDD: 00-006-0675). Sample grown at the milling times of 100 minutes (C-100) consisted of fullerene-C_{70} carbon phase (C- ICDD 00-048-1449), showing intense XRD peak at $2\theta = 23.90°$ with crystallographic parameters of $a = b = 0.98095$ nm, $c = 2.70220$ nm, and $\alpha=\beta= 90°$, $\gamma=120°$. It is known that fullerene-C_{70} enclosing seventy carbon atoms has a spherical caged structure made of 25 hexagons and 12 pentagons connected by single and double covalent bonds. Due to this unique structure of fullerenes, strong internal reflections occur in the spherical cage, thus enabling it a gifted MW absorber. Earlier studies indicated that fullerene being one of the efficient reinforcing materials can be greatly effective in absorbing MW radiation[27]. In addition, it was claimed that the graphite – fullerene composites can exhibit excellent MW absorption performance compared to pure graphite [28] which needs further validation.

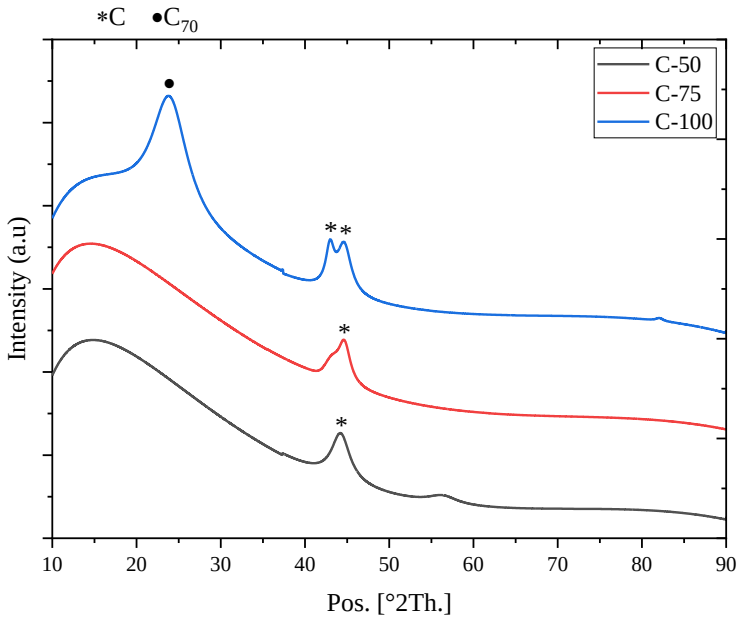

Fig. 2. XRD patterns of the as-prepared C-50, C-75, and C-100 samples with indicated carbon phases of ∗ C and ● C_{70}

3.3. Specific surface area and pore diameter of the activated carbon

Fig. 3 illustrates a multi-point isothermal BET plot of the activated carbon samples. Brunauer, Emmett, and Teller (BET) methods were applied to evaluate the specific surface area (m^2/g) of the samples (Table 1). These specific surface areas were used to determine the diffusion process through the porous material and selectivity for the catalyst reaction explained using the adsorption theory. The BET equation was used on the adsorption isotherms with P/P_0 values ranging from 0.05 to 0.3. The isothermal BET equation can be written as:

$$\frac{1}{W\left(\frac{P_0}{P}\right)-1} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C}\right]\frac{P}{P_0} \qquad (6)$$

where W denotes the volume of absorbed gas at the relative pressure P/P_0, V_m is the volume of nitrogen gas that formed a monolayer at a solid surface, P is the pressure of adsorption equilibrium, P_0 is the pressure of adsorption saturation and C is the constant of energy.

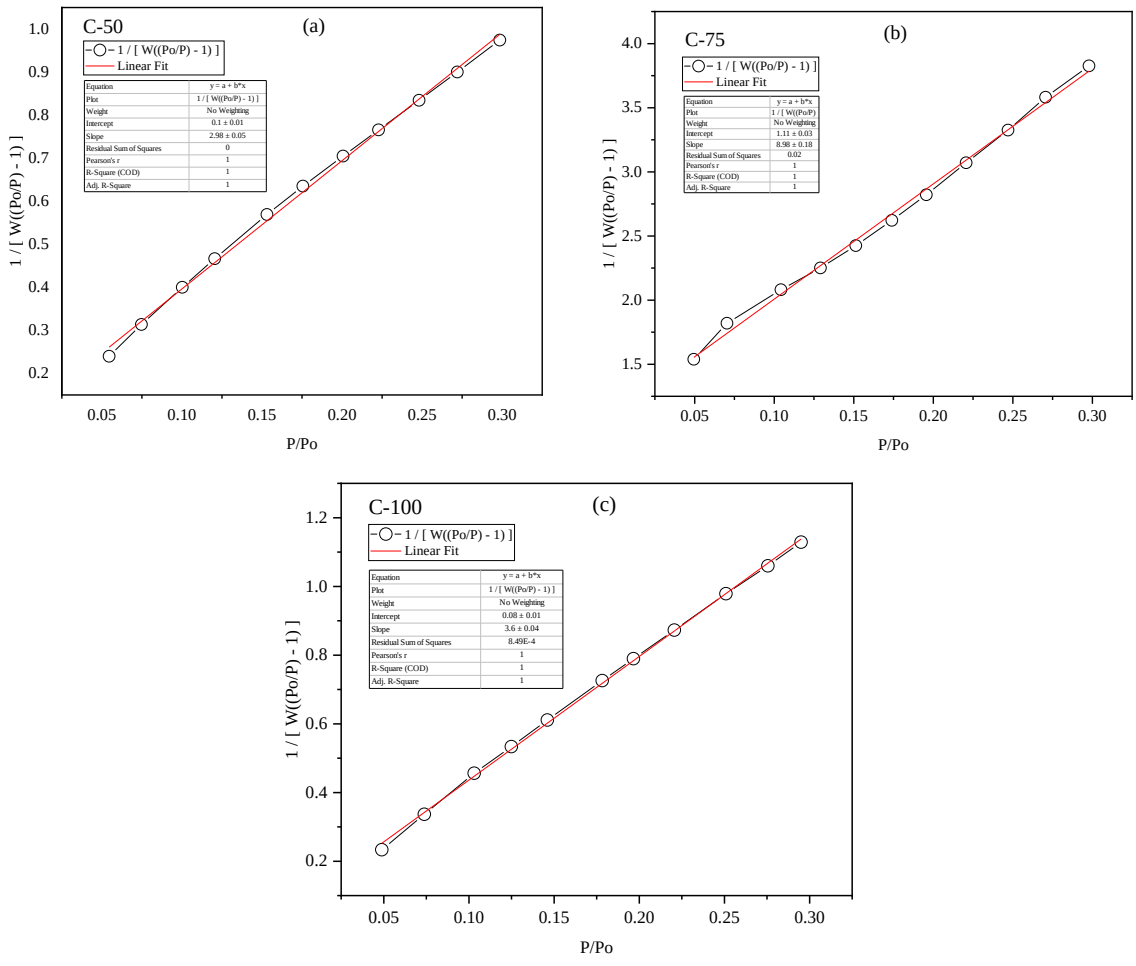

Fig. 3. Multi-point isothermal BET plot of all activated carbon specimens

The values of V_m for all the samples were estimated from the slope (s) and intercepts (i) on the BET chart, achieving the specific surface areas of the produced activated carbon given by:

$$s = \frac{C-1}{V_m C} \quad (7)$$

$$i = \frac{1}{V_m C} \quad (8)$$

Combining Eq. 7 and 8, one obtains:

$$V_m = \frac{1}{s+i} \quad (9)$$

The BET method was used to calculate the surface area of the sample (defined as the number of pores in each unit area of the sample). The specific surface area (S_{BET}) was estimated using:

$$S_{BET} = \frac{V_m N A_{cs}}{M} \quad (10)$$

where N is the Avogadro's number (6.023×10^{23} mol^{-1}), A_{cs} is the area of cross-section (16.2 Å) and M is the molecular weight (28.013 g/mol) of nitrogen.

Table 1. The specific surface area of the activated carbons

Sample Code	Slope (s)	Intercepts (i)	The volume of nitrogen gas (V_m)	Specific surface area S_{BET} (m^2/g)
C-50	2.980	0.098	0.325	1131.617
C-75	8.984	1.109	0.099	345.102
C-100	3.605	0.075	0.272	946.499

Fig. 4 depicts the Barret Joyner Hallenda (BJH) pore size distribution - nitrogen adsorption at 77.35 K for C-50, C-75, and C-100 samples. Irrespective of the milling times, the pore radius distribution of the samples was in the range of 1 and 250 nm wherein the maximum peaks occurred at 1.53 (for C-50), 1.94 (for C-75), and 1.71 nm (for C-100). The average pore diameters of C-50, C-75, and C-100 samples were 3.06, 3.88, and 3.42 nm, respectively. According to the International Union of Pure Applied Chemistry (IUPAC) standard, the resulting pore diameters were classified as mesopores (pore diameter range of 2-50 nm). In addition, the pore volumes of C-50, C-75, and C-100 samples were 1.02×10^{-6}, 6×10^{-8}, and 7.4×10^{-7} m^3/g, respectively.

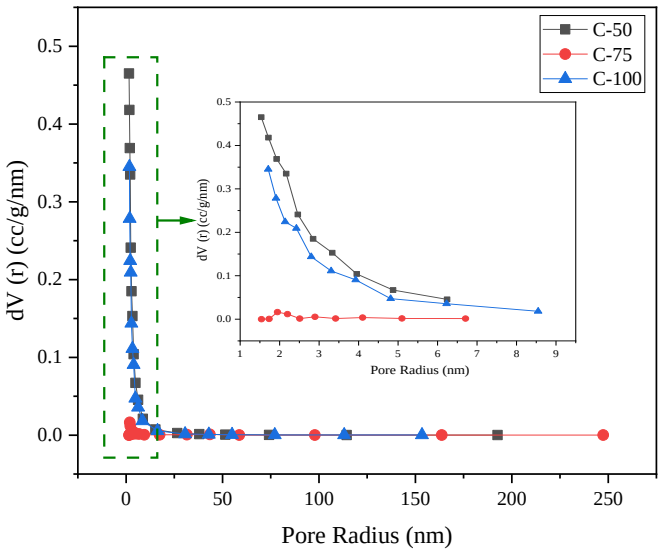

Fig. 4. BJH pore size distribution – nitrogen adsorption at 77.35 K for all activated carbon samples

Figs. 3 and 4 clearly revealed the activated carbon samples have a large specific surface area and excellent porosity. This porous morphology plays a significant role in the MW absorption, where a decrease in the pore diameter can appreciably increase the material's density or cavity concentration, thus leading to an alteration in the specific surface area responsible for the MW absorption. Consequently, an improvement in the specific surface area and porosity of the samples enables more interaction between carbon atoms and MW on the surfaces and interfaces.

2.3. Relative complex permeability and permittivity of the activated carbon

Fig. 5 displays the relative complex permeability and permittivity of C-50, C-75, and C-100 samples measured in the frequency range of 8.2-12.4 GHz. It is worth noting that the real permeability values of C-50, C-75, and C-100 samples were comparable due to their almost similar crystal phases. Conversely, the C-100 sample showed higher magnetic energy storage capacity (higher value of real permeability) than the C-50 and C-75 samples. Irrespective of the milling times, the real permeability values for all samples were gradually decreased to zero with the increase of MW frequency (Fig. 5(a)). The imaginary permeability of the C-100 sample (Fig.

5(b)) was related to magnetic loss which dropped significantly to almost zero in the range of 8.2 to 9 GHz and then fluctuated near zero. Meanwhile, the real permittivity of C-50 and C-75 samples (Fig. 5(c)) exhibited gradual declination trends with the increase in frequency. However, the real permittivity of the C-100 sample remained steady with the increase in frequency, indicating an excellent electrical field energy storage performance of C-100. The real permittivity (or dielectric constant) also determines how much the incoming energy can be reflected and absorbed by the proposed activated carbon. In the frequency range of 8.2 to 9.3 GHz, the imaginary permittivity (or dielectric loss factor) of C-100 sample was negative (Fig. 5(d)), indicating an electrical field energy storage in the material rather than dissipation. In addition, the electrical dipole polarization-enabled dielectric loss factor of the activated carbon specimen up to 9.3 GHz was mainly governed by the dominant heating mechanism or electrical field energy dissipation in the form of heat inside the material. It is important to note that the dielectric polarization not only depended on the strength of the applied electric field but also the geometry or crystal structure of the proposed activated carbon specimen.

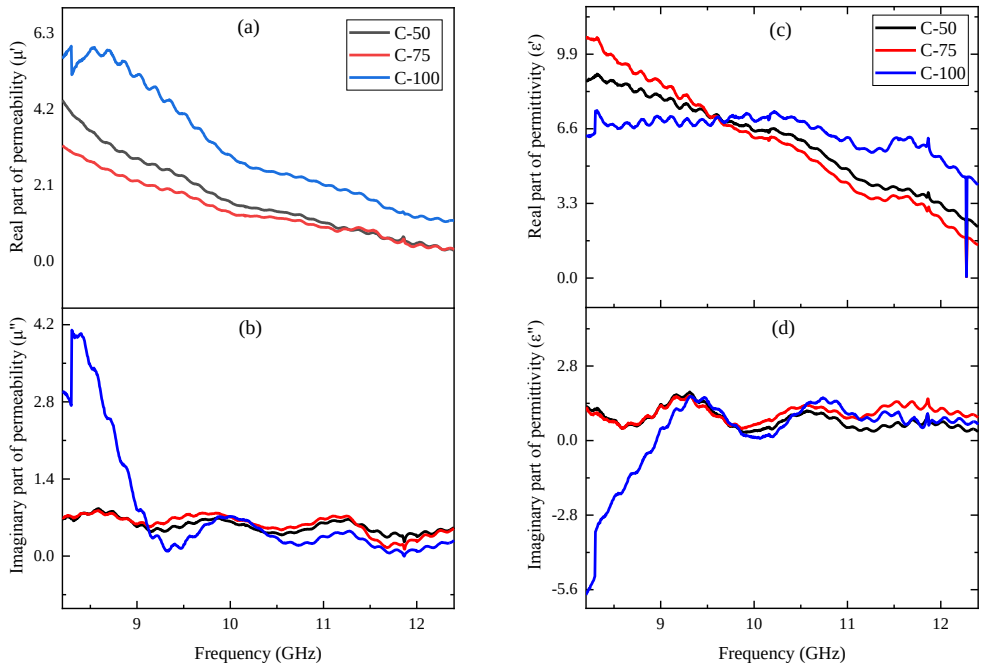

Fig. 5. MV frequency-dependent relative complex permeability and permittivity of 4 mm thick activated carbon.

2.4. Microwave reflection loss of activated carbon

Fig. 6 illustrates the MW absorption properties of all activated carbon specimens in terms of their frequency-dependent reflection loss (R_L). The R_L was found to be controlled by adjusting the milling time. The patterns of R_L for C-50 and C-75 were similar with an average value of approximately -10 dB. Conversely, the C-100 sample exhibited a prominent absorption band around 9 GHz with a bandwidth of 3 GHz. Interestingly, a mesoporous C-100 sample containing fullerene-C_{70} revealed significant MW absorbance in the X-band, indicating its potential for MW X-band applications in electronic devices. The produced fullerene-C_{70} dominated activated carbon also showed outstanding permeability and permittivity, suggesting its appropriateness for the MW X-band applications. Furthermore, the occurrence of a weak oscillation in the high-frequency range was attributed to the internal surface reflection within the mesopores. It was asserted that the milling process with optimal milling time could substantially enhance the microwave absorption capacity of the activated carbon. In short, the suggested fullerene-C70 enclosed activated carbon can lead to the development of low-cost, high-efficiency MW absorption materials desired for sundry applications.

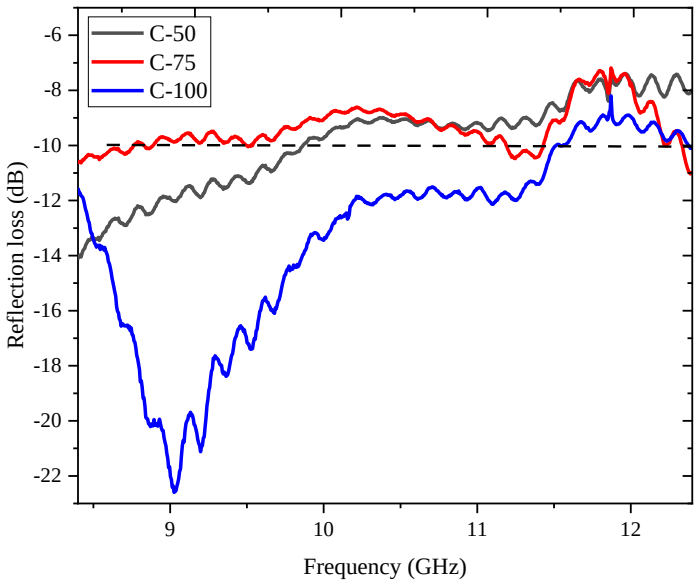

Fig. 6. MW reflection loss as a function of frequency for all activated carbon specimens of 4 mm thick.

4. Conclusions

For the first time novel activated carbon specimens (C-50, C-75, and C-100) were prepared from the coconut shells using a modified milling process plus a heating process. The milling times were varied (50, 75, and 100 minutes) to get mesoporous activated carbon with improved MW absorption properties. The surface morphology, phase, structure, surface area, porosity, and MW reflection loss of these samples were improved with the increase in milling times. Activated carbon obtained at a milling time of 100 minutes was the optimum one in terms of structures, morphology, and MW absorbance. The C-100 sample showed a phase transformation from cubic to the rhombohedral crystal structure (or fullerene-C_{70}). The specific surface area and mean pore diameter of the C-100 specimen were 946.499 m^2/g and 3.42 nm, respectively. The activated carbon-containing fullerene-C_{70} revealed excellent permeability and permittivity characteristics suitable for MW X-band applications. It was affirmed that by regulating the surface area and fullerene-C_{70} contents in the activated carbon the MW reflection loss can be tuned. The proposed fullerene-C_{70} based activated carbon can lead to the development of cheap and efficient MW absorption materials required for varied purposes.

Acknowledgments

The authors are grateful to the Universitas Jenderal Soedirman (Contract number: T/573/UN.23.18/PT.01.03/2021) and UTM Malaysia (UTMFR 20H65) for their financial assistance.

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- Fullerene-C_{70} enriched activated carbon was derived from coconut shells via a customized milling process.
- Prepared activated carbon showed high porosity and large specific surface area effective for MW X-band applications.
- Produced activated carbon revealed improved MW reflection loss due to the presence of fullerene-C_{70}.
- Structure, morphology, and MW reflection loss of the activated carbon were analyzed.
- Specific surface area, porosity, and fullerene contents were shown to be tuned by increasing the milling times.

Graphical abstract