UNIVERSITI
MALAYSIA
PERLIS

UniMAP

Textural and Adsorption Analysis of Nanocarbon Particles

Syazwani Zainal Abidin[1], Imran Syakir Mohamad[1,2], Ahmad Yusairi Bani Hashim[3], Norli Abdullah[4], Amirah Abdullah[1]

[1]Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[2]Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[3]Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
[4]Centre for Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia.

ABSTRACT

In this present work, the characterization of the nanocarbon material which is multi-walled carbon nanotube (MWCNT) and carbon nanofiber (CNF) was investigated using nitrogen gas adsorption technique, Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM). The characterization testing was performed to study the surface species of the materials which including morphology and specific surface area (pore type, pore volume, surface area). Three nanocarbon were characterized in this research which is 1) MWCNT-OH, 2) Modified MWCNT and 3) Commercial CNF. The porosity existence of this nanocarbon was analyzed by using BET method and the surface area is measured by diameter and depth of the existed pores. A comparative study of the adsorption shows that all the nanocarbon isotherm can be classified as Type IV which generally associated with mesoporous adsorbents. Density Functional Theory (DFT) plot which calculates the porosity population revealed the existence of micropore and mesopore for all the tested sample. Meanwhile, the BET surface area reading shows that MWCNT-OH has the largest surface area (MWCNT-OH > Commercial CNF > Modified MWCNT) compared to other nanocarbon. Pore volume plays a significant role in affecting the BET surface area as the MWCNT-OH has the largest pore volume which contributes to the high surface area. The morphology and functionalized-group attachment on the nanocarbon surface was characterized using FESEM and FTIR. All the FESEM images demonstrated agglomerate carbon nanotube and nanofibers, primarily with non-uniform tubular structure. FTIR spectra revealed that the Modified MWCNT gives the highest hydroxyl group –OH with the value of 3442 cm^{-1} peaks followed by MWCNT-OH and Commercial CNF. Overall, this finding generated a great interest in studying the properties of surface porosity and particle size for materials engineering.

Keywords: Adsorption, Nanocarbon, Characterization.

1. INTRODUCTION

Recent trends in materials fields have prompted to a proliferation of carbon as the leading material in an extensive variety of uses due to its low cost, high electrical conductivity, good chemical stability, ecologically friendly and long-life range [1]. The synthesis and utilization of feasible carbon materials are receiving increasing levels of interest, especially as application

advantages with regards to future energy/chemical industry are getting to be perceived [2]. Carbon has long been a question of great interest in a wide range of fields as for example in electrical applications, the commercial activated carbons (ACs) restrain the invention of a high-quality performance of capacitor due to the limitation of the specific surface area, conductivity, pore size distribution and porosity [3]. Recent developments in the field of carbon materials have led to a renewed interest in carbon nanotubes (CNT) or nanofiber (CNF). CNT or CNF have been the focus of extensive study by many researchers because of their amazing strength along with excellent mechanical, electrical, thermal and magnetic properties [4]. The large surface area and small size of nanocarbon particles have marked these materials to be desirable for various applications. However, the selection of nanocarbon materials to be used in device manufacture, the crucial consideration should be fitness for tenacity having regard to the characteristics and properties of the material, which includes biochemical, toxicological, physical, electrical, morphological and mechanical properties [5]. Thus, primarily to appraise these concerns, it is essential to conduct chemical, morphological and physical testing as a part of a materials characterization.

The characterization of nanocarbon material is useful for evaluating physical and chemical properties of materials that are a crucible for process or reaction performance. The characterizations of nanocarbon can provide information on material handling and behavior within any process. This paper will introduce to the reader the most recent and important progress regarding the characterization of nanocarbon, whilst also highlighting the overview of the significance of materials characterization and the variety of relevant test methods. Thus, this research aimed to study the surface species of the materials which including morphology and specific surface area (pore type, pore volume, surface area) to yield essential information in studying the properties of surface porosity and particle size for materials commerce.

2. METHODOLOGY

2.1 Materials and Methods

The characterization testing was performed on this selected nanocarbon which are MWCNT-OH, Modified MWCNT and Commercial Carbon Nanofiber (CNF). The MWCNT-OH used in this research is the industrial grade multiwalled CNT that has been functionalized with –OH, purchased from Nanostructured & Amorphous Materials, Inc. (Nanoamor). Whilst, the Modified MWCNTs were purchased from a major producer in China, which the raw CNTs products have been processed and purified through chemical treatment using the nitric acid (HNO_3) oxidation techniques. For nanofibers, CNF used in this research is from Pyrograf III Carbon Nanofiber, High Heat Treated 24 (HHT24) grade. HHT indicates the high heat treatment which this CNF is heated up to 3000°C [6]. Carbon nanofibers are available in a free-flowing powder form which typically 99% mass is in a fibrous form. Table 1 describes the properties of the three selected nanocarbon.

Table 1 Properties of nanocarbon

Nanocarbon Types	Outer Diameter, OD [nm]	Specific Surface Area [m²/g]
MWCNT-OH	10-30	100
Modified MWCNT	30-50	60
Commercial CNF	100	43

Autosorb 6-B surface area and pore size analyzer machine manufactured by Quantachrome Instruments were used for textural characterization of this nanocarbon. The samples must be

degassed for 7 hours at 120°C to remove moisture and vapor. Then, samples were weighed after the process before continuing with N_2 physisorption analysis by measuring the volume of nitrogen gas adsorbed at the specific pressures. For morphological examinations of the nanocarbon sample, an FEI Quanta 200F Field Emission Scanning Electron Microscopy (FESEM) was used. All the resolution images were obtained with an acceleration voltage of 5 kV and 12 kV. FTIR spectra were performed using PerkinElmer Spectrum 100 FTIR spectrometer. All the spectra recorded were processed with the computer software program Spectra for Windows (Perkin-Elmer).

3. RESULTS AND DISCUSSION

3.1 Textural Characterization

The nitrogen gas (N_2) adsorption analysis was done generally focused on the ability of absorbent features for characterization properties influenced by porosity and texture development of nanomaterial [7]. The porosity existence is analyzed by using BET method through the adsorption and desorption techniques by applying gas or steam as an adsorbate. A graph of volume against relative pressure for each sample was plotted to visualize the adsorption isotherm as shown in Fig. 1, Fig. 2 and Fig. 3. The information related to the shape, type of porosity and depth of existed pores in the samples can be gained from the isotherm plot. From the figure, the isotherm is divided into three regions. The first region is derived from 0 - 0.3 P/P_o relative pressure, second 0.3 - 0.75 P/P_o and third region fall in the range of 0.75 - 1.0 P/P_o.
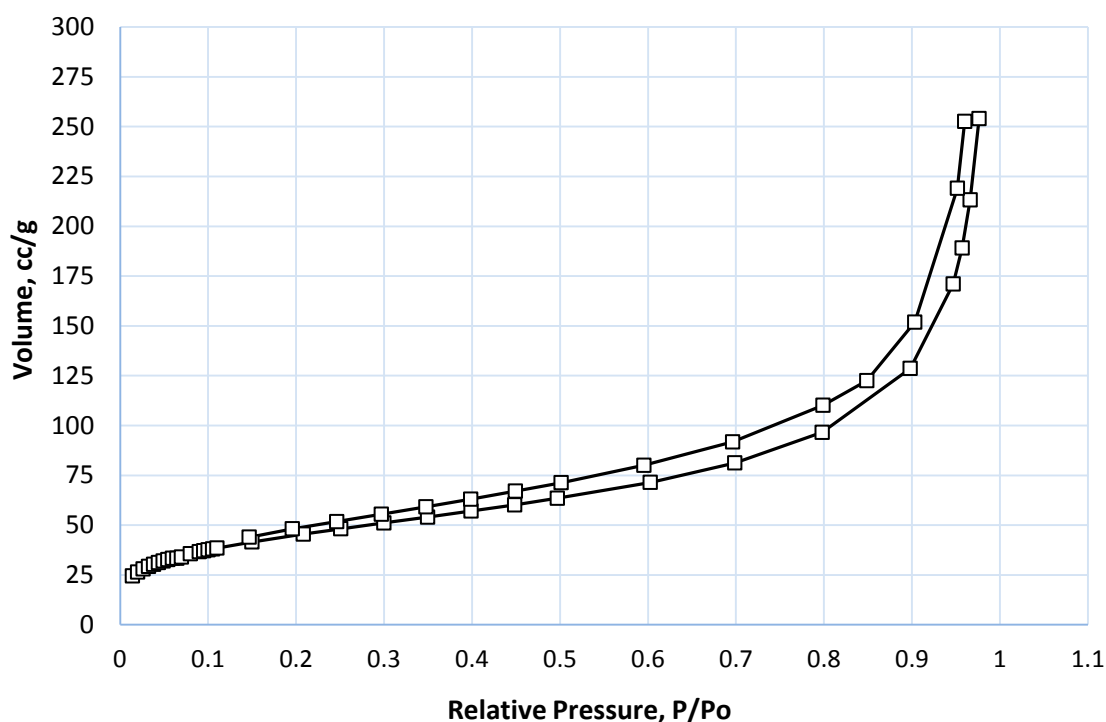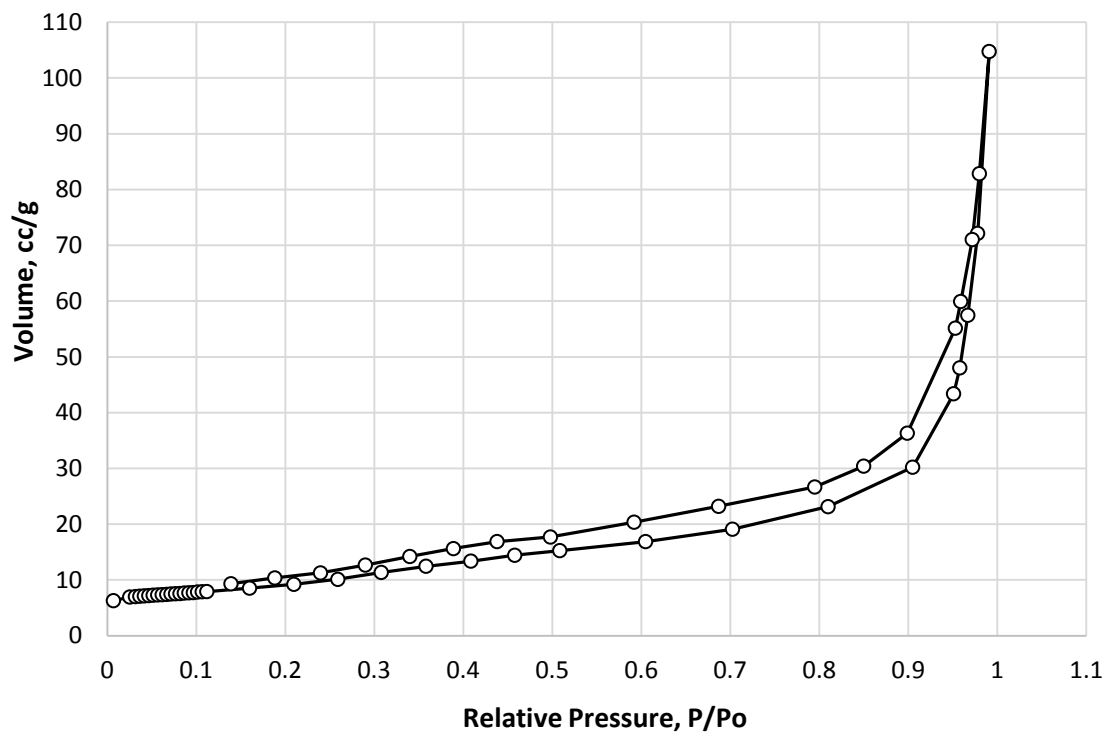

Figure 1. MWCNT-OH isotherm.
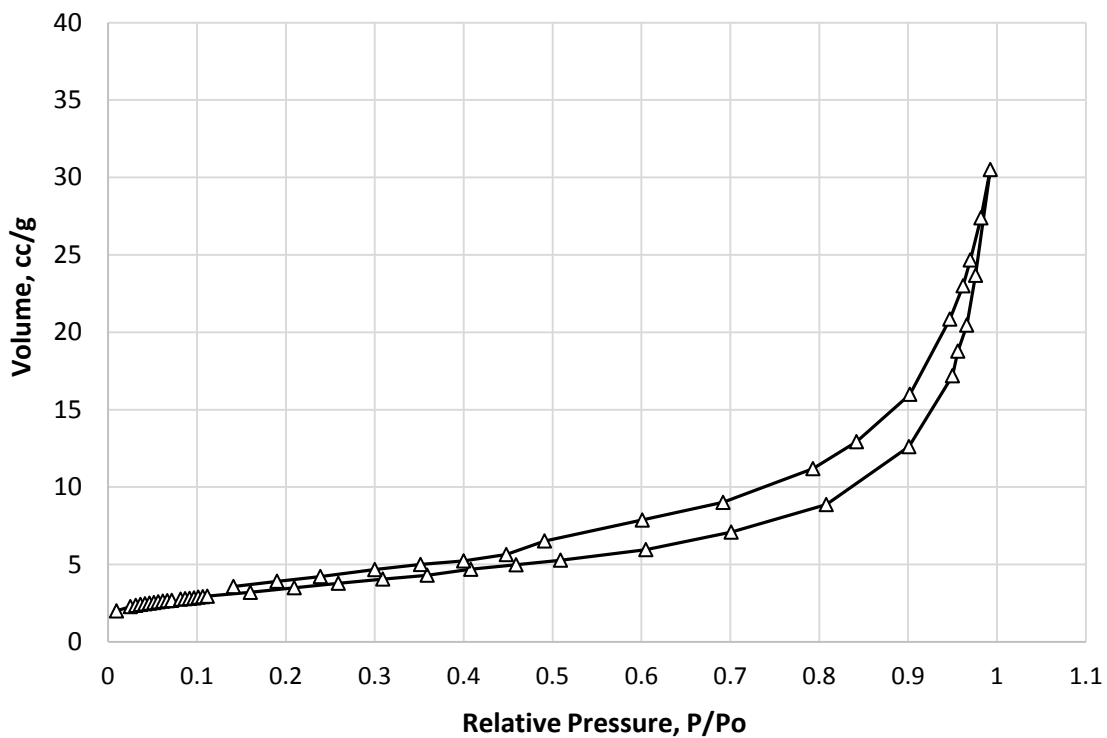
Figure 2. Commercial CNF isotherm.

Figure 3. Modified MWCNT isotherm.

Referring to Fig. 1, Fig. 2 and Fig. 3, all the nanocarbon isotherm can be classified as Type IV. MWCNT-OH has a high adsorption uptake at low relative pressure (P/P$_o$) which indicates the presence of abundant micropores. The adsorption amount increases progressively and still do not reach a plateau close the P/P$_o$ of 1.0, demonstrating the presence of mesopores [8]. The Type IV characteristics isotherm shape is generally associated with mesoporous adsorbents. The mesopore capacity is the amount adsorbed at the plateau and the mesopore volume is then obtained by assuming the condensate density to be that of liquid nitrogen. Isotherm Type IV is characterized by hysteresis loop showing the presence of capillary condensation turned in a mesoporous material. Isotherm is not limited to a monolayer adsorption at the adsorbent surface, or otherwise, it is also can occur on adsorption multilayer. Capillary condensation is very often conveyed by hysteresis. It can be seen clearly from the graph that there is the presence of hysteresis type H4 in this sample. H4 hysteresis loops are generally observed with complex materials containing both micropores and mesopores. Both, types H3 and H4 hysteresis contain a characteristic step-down in the desorption branch associated with the hysteresis loop closure [9]. These results agree with those reported by [10] as his novel studies on hierarchical porous nitrogen-doped carbon nanosheet (HPNC-NS) shows a strong nitrogen adsorption of type IV isotherm. The findings also revealed that there is the existence of micro and meso in HPNC-NS.

Materials with micro-sized pores show the strong interactions among the narrow pore walls with material adsorbed on the relative pressure which causes the volume of material adsorbed in the pores increases [11]. Pore with meso sized shows an increase in the volume of the adsorption because of the occurrence of capillary condensation turn through the establishment of a hysteresis loop. Macro-sized pores indicate the formation of a monolayer on relatively at low pressure and the adsorption layers at relatively high pressure. Material which has bigger pore will result in a weak interaction between materials adsorbed and the adsorbent which causing difficult adsorption. The isotherm was figured out from curve slope and adsorption point placement. Therefore, the acquisition surface area reading is supportive of isotherm assessment and further evaluation was proven by Fig. 4 of DFT plot which covering all type of pores of tested sample features. Density Functional Theory (DFT) is the best evidence to clarify an existence of porosity type and elucidating the distribution of porosity population. Generally, DFT pore size distribution method calculates the distribution of micro, meso and macropores from an adsorption isotherm. The micropore diameter size is between 0 nm to 2 nm, mesopore is between 2 nm to 50 nm and macropore size is more than 50 nm. For each sample, a graph of pore volume against pore width as shown in Fig. 4 were plotted to visualize the pore size distribution.
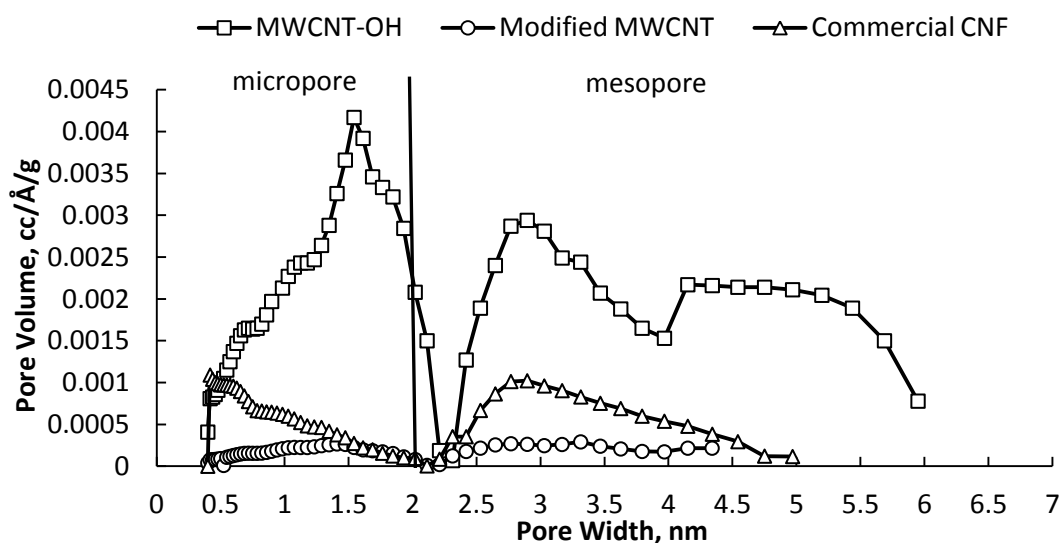

Figure 4. DFT pore size distribution comparison.

Referring to the Fig. 4, the plot for MWCNT-OH shows that the high peak is representing a range of micropore type with diameter 1.4 nm and depth 2.15×10^{-2} cc/g which shows that MWCNT-OH has a high distribution of micropore-type and average distribution of mesopores. For Modified MWCNT, the plot shows that high peak is representing a range of mesopore type with diameter 3.1 nm and depth 5.25×10^{-3} cc/g. Whilst, Commercial CNF also shows the high peak with a high distribution of mesopores which have 0.39 nm and depth 2.07×10^{-4} cc/g with a moderate distribution of micropores. Carbon particles which contain numerous micropores with condensed and loose aggregation will lead to mesopores and macropore [8]. Considering that fact, thus the classification of pores is very significant because porous materials with the same likely porosity, but with different size and shape of pores might react in a different way under the same circumstances. For example, the highly porous carbons are generally been used as electrode materials in electric double-layer capacitors (EDLC) as the meso/macroporous carbons promote the formation of an effective double layer or the transfer of ions into the pores. This situation resulting in the increase in the electrolyte wettability and rate capability [12]. Surface area is measured by diameter and depth of existed pores and the reading are based on the volume of gas adsorbed. Table 2 summarizes the BET surface area, pore diameter and pore depth for all the nanocarbon.

Table 2 BET surface area, pore diameter, and pore depth

Nanocarbon	BET Surface Area [m²/g]	Pore Diameter [nm]	Pore Depth [cc/g]
MWCNT-OH	1.610×10^2	1.4	2.15×10^{-2}
Modified MWCNT	1.261×10^1	3.1	5.25×10^{-3}
Commercial CNF	3.241×10^1	0.39	2.07×10^{-4}

MWCNT-OH which have 10-30 nm OD that was purchased from Nanoamor had a measured BET surface area of 1.610×10^2 m²/g. This was compared with Commercial CNF sample which had a BET surface area of 3.241×10^1 m²/g, while the Modified MWCNT had the lowest BET surface area of 1.261×10^1 m²/g. The BET surface area obtained shows that MWCNT-OH has the largest surface area (MWCNT-OH > Commercial CNF > Modified MWCNT) compared to other nanocarbon. It was noted that pore volume plays a significant role in affecting the BET surface area as shown in Fig. 4. From the DFT plotted graph, it is clearly seen that MWCNT-OH has the largest pore volume (MWCNT-OH > Commercial CNF > Modified MWCNT) when compared to others. Theoretically, the surface area of a solid varies as the square of its dimensions, whereas the volume of a solid varies as the cube of its dimensions. High distribution of micropores will contribute to the high specific surface area [13]. Therefore, smaller particles will tend to have a larger surface area to volume ratios than the larger particles. In contrast, all the nanocarbon may have a similar dimension, but with differing porosities, it may have contributed to different surface areas.

FESEM analysis is valuable for visualizing and measuring macroscopic features up to the nanoscale dimension. Fig. 5 shows the morphology of the three nanocarbons. From the FESEM images, the morphology of the three different nanocarbons is clearly distinguished from each other. FESEM images of MWCNT-OH and Modified MWCNT demonstrates that the morphology is quite similar, however, there is a huge difference in BET surface area results as Modified MWCNT had the lowest BET surface area. The probable reason for the low result for Modified MWCNT was attributed to a large number of impurities [13]. Generally, from the FESEM images, the nanotubes morphology is randomly entangled and highly interconnected, probably due to the van der Waals forces. Whilst, the structural properties of Commercial CNF convert the fibre to a fully graphitized form and creates a highly conductive carbon nanofiber. The properties that

found to influence surface area were several walls or diameter, impurities, and surface functionalization with hydroxyl and carboxyl groups [14].
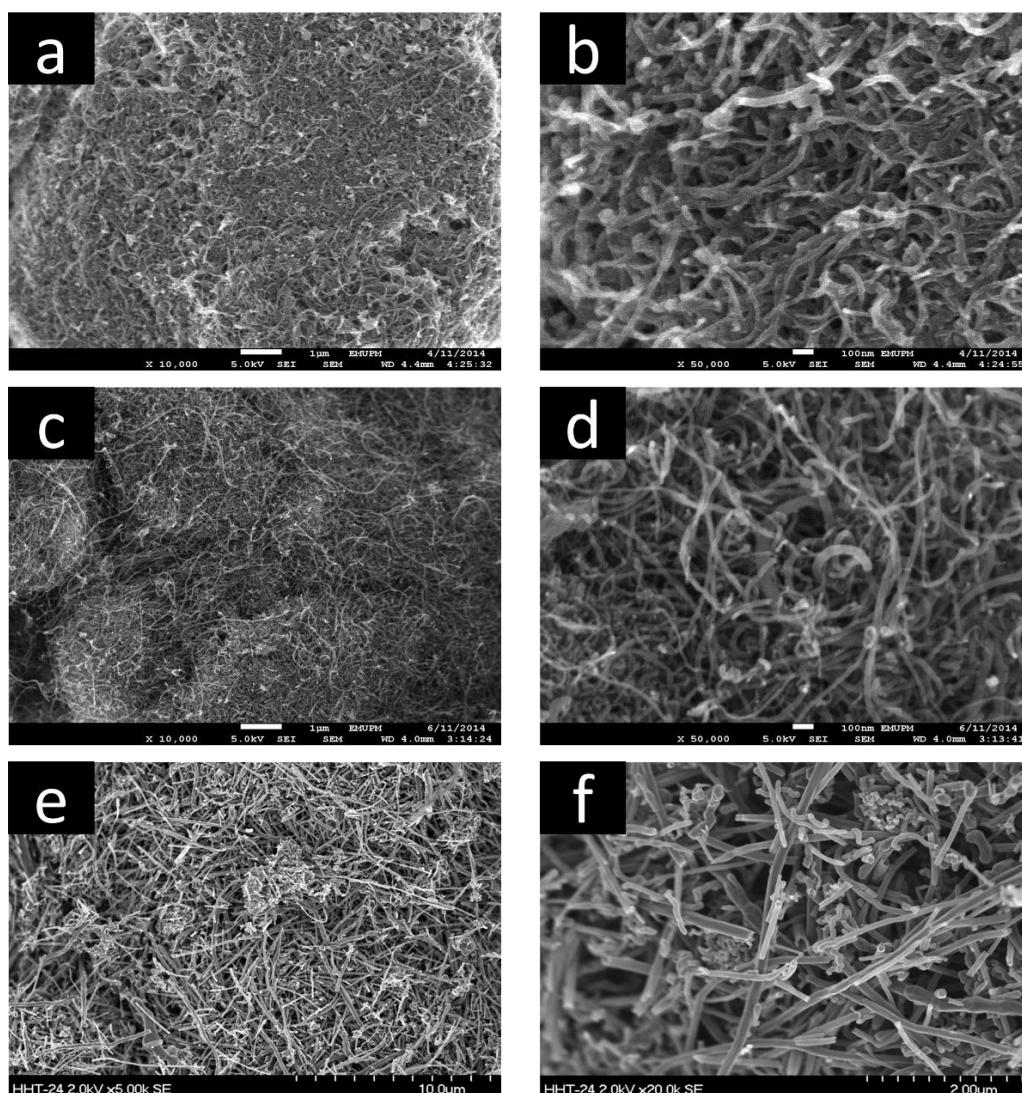
Figure 5. FESEM images of all nanocarbon (a, b) MWCNT-OH, (c, d) Modified MWCNT and (e, f) Commercial CNF.

3.2 Functional Group Characterization

Fig. 6 shows the plotted FTIR spectra of the nanocarbon. On the horizontal axis is the infrared wavelengths expressed in term of a unit called wavenumber (cm⁻¹) which represents the number of waves fit into one centimeter. Each FTIR spectrum represents the surface oxygen and alkene functional group that are present in the nanocarbon.
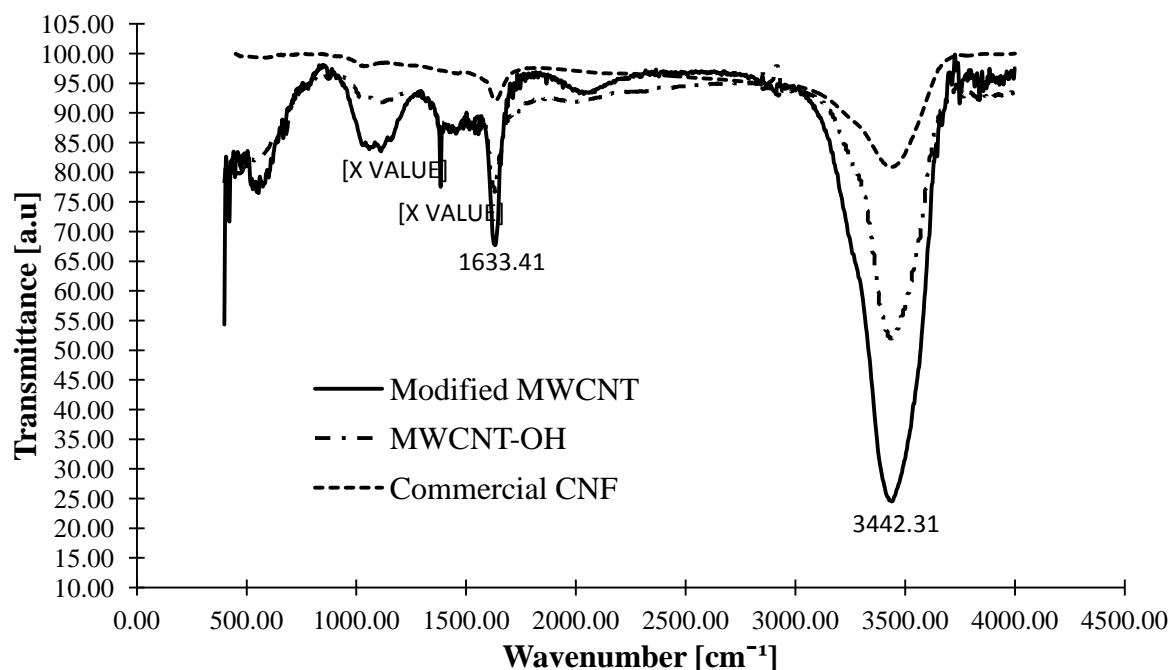
Figure 6. FTIR spectra of MWCNT-OH, Modified MWCNT, and Commercial CNF.

FTIR spectra of the CNTs reveal that the Modified MWCNT gives the highest hydroxyl group – OH (3442 cm^{-1}) peak followed by MWCNT-OH and Commercial CNF. Modified MWCNT has the highest -OH peak due to the functionalization of the molecule with –OH group.

The peak at 1633 cm^{-1} associated with C=C stretching in aromatic nanocarbon. Meanwhile, peak at 1384 cm^{-1} shows a presence of C-H bond and peak in 1049 cm^{-1} shows a presence of C-O bond. The frequency range 500 to 1500 cm^{-1} is known as the fingerprint region. The fingerprint region shows that the sample being tested contains very specific structure for each compound or molecule. Functionalization of CNTs may take place through a variety of treatments as Naseh et al. [15] highlights that the chemical and plasma functionalization of MWCNTs increases the specific surface area of the MWCNTs.

3.3 Influence of Nanocarbon Properties on Specific Surface Area

The diverse properties of nanocarbon can give impact to the surface areas of CNT or CNF. The surface area of nanocarbon was influenced by the several factors which are the number of walls, tube diameter, surface functionalization and also metal and amorphous carbon [16]. The synthesis method used by the manufacturer to produce nanocarbon may also contribute to the varying surface area, however, this specific parameter was not a critical part to be addressed. When discussing the nitrogen adsorption on nanocarbon, nitrogen adsorption has occurred at the multiple surfaces of the typically bundled CNTs [17]. Nitrogen adsorption may happen at the outside surface of the curved portion of a CNT or in a groove site, which is formed by the two-contiguous bundle of CNT [13]. Nitrogen can likewise adsorb to the inward center of a CNT, if possible and the interstice space between three or more CNTs in a bundle [18]. Nitrogen has a kinetic diameter of 3.64 Angstrom [19] which permitted the nitrogen adsorption to happen on both outsides and inside the CNTs, aside from the spaces between the layers of MWCNTs, which are accounted to be around 3.4 Å [20]. The important consideration when comparing specific surface area is to take account whether the tubes are open or closed [13]. In accordance with the studies, these statements are consistent with those of other studies and suggest that the tubes are all open and some may close.

300

Conversely, a broader perspective has been reported by other researchers which concluded that the production process such as synthesis, purification and functionalization will cause the CNT tube to open or close [21]. Classically, CNTs tube are closed on the ends before been treated for purification or functionalization which then open the ends of the CNTs to varying degrees [13]. An extensive variety of CNTs specific surface area values has been reported by many scientists, which relies on numerous variables, for example, synthesis method, purging techniques, and chemical and physical properties. Zhu et al. [22] reported in his studies the specific surface area for MWCNTs are from 22.38 m^2g^{-1} to 1670 m^2g^{-1} as reported by Raymundo-Pinero et al. [23]. The low value for MWCNTs was due to the high amount of impurities in the nanocarbon, meanwhile, the high value is ascribed to the bigger porosity which effects from chemical activation of scattered MWCNT sample orchestrated by CVD method. Numerous studies have reported the wide range of specific surface area of CNTs with common values of ~150 to 600 m^2/g for SWCNTs [24] and from ~15 to 300 m^2/g for MWCNTs [25].

Significantly, different properties of CNTs produced by difference manufacturer may influence the specific surface area of the tested sample. The CNTs product may undergo a varying treatment by the manufacturer but offer the same CNT properties. An MWCNT-OH from Nanoamor [10-30 nm OD] had a BET surface area of $1.610x10^2$ m^2/g, while a Commercial CNF [100 nm OD] from Pyrograf III Products had a BET surface area of $3.241x10^1$ m^2/g. Modified MWCNT [30-50 nm OD] had a BET surface area of $1.261x10^1$ m^2/g, which is much lower than the other materials. Clearly, the specific surface area of CNTs from various suppliers may show an extensive variety of qualities (Table 2). Diverse preparing techniques used by various makers impact imperative elements, for example, tube packaging, part of open tubes, and the sums and sorts of contaminations present, adding to the changing of a specific surface area of these materials.

Functionalization of CNTs may happen through a range of treatment such as with -OH and -COOH functional groups. Naseh et al. [15] comparative study found that chemical and plasma functionalization of MWCNTs will increase the specific surface area of the MWCNTs. The brief explanation to explain this is due to the functionalization process which will open tube ends and creates sidewall defects which provide accessibility into the hole of the CNTs, therefore increasing specific surface area [13]. The surface area results which was discussed in this paper are for –COOH and –OH functionalized CNTs, however, it is conceivable that functional groups other than those predefined by the producer are available. As from the FTIR results, the –OH functionalization made no noteworthy change in BET surface area. Un-functionalized material which is Commercial CNF had a BET surface area of $3.241x10^1$ m^2/g, which is has a comparable result for carboxyl-functionalized (–COOH) MWCNTs (Modified MWCNT) with BET surface area of $1.261x10^1$ m^2/g. Surface functionalization with –OH delivered no huge contrast with respect to un-functionalized MWCNTs.

The best explanation to explain this is that the un-functionalized materials had undergone acid and heat treatments to obtain a highly-purified sample, removing metals and possibly opening nanotubes. In general, purification influences the specific surface area, thus when comparing a highly-purified material with a surface functionalized materials, there is no expectation to see a difference in the specific surface area because of the similar treatments [14].

4. CONCLUSION

The characterization testing for the nanocarbon materials was conducted to give a better understanding of the textural and surface properties of nanocarbon. Three nanocarbon were characterized in this research that is MWCNT-OH, Modified MWCNT, and Commercial CNF. All three nanocarbon were characterized using N_2 physisorption, FESEM, and FTIR. A comparative

study of the isotherm assessment shows that all the nanocarbon isotherm can be classified as Type IV which generally associated with mesoporous adsorbents. Density Functional Theory (DFT) plot which calculates the porosity population revealed the existence of micropore and mesopore for all the tested sample. Meanwhile, the BET surface area reading shows that MWCNT-OH has the largest surface area (MWCNT-OH > Commercial CNF > Modified MWCNT) compared to other nanocarbon. Pore volume plays a significant role in affecting the BET surface area as the MWCNT-OH has the largest pore volume which contributes to the high surface area. BET result obtained uses to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The morphology of all sample tested using FESEM shows that the nanocarbon is randomly entangled and highly interconnected, probably due to the van der Waals force interaction. All the FESEM images illustrated agglomerate carbon nanotube and nanofibers, primarily with non-uniform tubular structure. From FTIR result, the spectra reveal that the Modified MWCNT gives the highest hydroxyl group –OH with the value 3442 cm^{-1} peaks followed by MWCNT-OH and Commercial CNF. This characterization method allows the advance research of the sample tested by quantify the graphitic content of the nanocarbon and characterize the atomic structure which cannot be studied in a conventional method. Besides, the sample used also can be improved by studies a large variety of commercial nanocarbon that has on the market nowadays. Each nanocarbon might have different characteristics as it was produced by a different manufacturer. Thus, a more result would yield if more sample is being investigated. The investigation of the textural properties could also be revised by broadening the scope of research. In conclusion, the characterization of nanocarbon materials is essential to provide information on how the material should be used or why a material has a given behavior within a process. Overall, this finding generated a great interest in studying the properties of nanocarbon materials, morphology, surface porosity and particle size for materials engineering.

ACKNOWLEDGEMENT

REFERENCES

[1] Li, X., Chen, Y., Huang, H., Mai, Y.W., Zhou, L., Electrospun Carbon-Based Nanostructured Electrodes for Advanced Energy Storage-A Review. Energy Storage Materials. **5** (2016) 58-92.

[2] Titirici, M.M., White, R.J., Brun, N., Budarin, V.L., Su, D.S., del Monte, F., Clark, J.H., MacLachlan, M.J., Sustainable Carbon Materials. Chemical Society Reviews. **44**, 1 (2015) 250-290.

[3] Simon, P., Gogotsi, Y., Materials for Electrochemical Capacitors. Nature Materials. **7**, 11 (2008) 845-854.

[4] Mohamad, I. S., Chitrambalam, S. T., Imran Syakir, M. and S Thiru, C., 2012. Investigations on the Thermo-Physical Properties of Nanofluid-Based Carbon Nanofibers Under Modified Testing Conditions. Int. J. Nanoelectronics and Materials. **5**, 1 (2012) 25-30.

[5] Abidin, S.Z., Mohamad, I.S., Hashim, A.Y.B., Abdullah, N., Hafiz, M.I.M., Masripan, N.A.B., Abdullah, A., Investigation of Thermal Characteristics of CNF-based Nanofluids for Electronic Cooling Applications. Journal of Mechanical Engineering and Sciences. **10**, 3 (2016) 2336-2349.

[6]   Abidin, S.Z., Mohamad, I.S., Hashim, A.Y.B., Abdullah, N., Characterization of nanocarbon particles using nitrogen adsorption analysis: isotherm, pore type, pore size and BET surface area. Proceedings of Mechanical Engineering Research Day, (2016) 127-128.

[7]   Gadipelli, S., Guo, Z. X., Graphene-Based Materials: Synthesis and Gas Sorption, Storage and Separation. Progress in Materials Science. **69** (2015) 1-60.

[8]   Liang, Y., Wu, D., Fu, R., Carbon Microfibers with Hierarchical Porous Structure from Electrospun Fiber-Like Natural Biopolymer. Scientific Reports. **3** (2013).

[9]   Thommes, M., Physical Adsorption Characterization of Nanoporous Materials. Chemie Ingenieur Technik. **82**, 7 (2010) 1059-1073.

[10]   Hou, J., Cao, C., Idrees, F., Ma, X., Hierarchical Porous Nitrogen-Doped Carbon Nanosheets Derived from Silk for Ultrahigh-Capacity Battery Anodes and Supercapacitors. ACS Nano. **9**, 3 (2015) 2556-2564.

[11]   Schumacher, K., Ravikovitch, P. I., Du Chesne, A., Neimark, A. V., Unger, K. K., Characterization of MCM-48 Materials. Langmuir. **16**, 10 (2000) 4648-4654.

[12]   Shiraishi, S., Kurihara, H., Shi, L., Nakayama, T. and Oya, A., Electric Double-Layer Capacitance of Meso/Macroporous Activated Carbon Fibers Prepared by the Blending Method. J. Electrochem. Soc. **149**, 7 (2002) A855-A861.

[13]   Birch, M. E., Ruda-Eberenz, T. A., Chai, M., Andrews, R., Hatfield, R. L., Properties That Influence The Specific Surface Areas of Carbon Nanotubes and Nanofibers. Annals of Occupational Hygiene. **57**, 9 (2013) 1148-1166.

[14]   Centrone, A., Brambilla, L., Renouard, T., Gherghel, L., Mathis, C., Müllen, K., Zerbi, G., Structure of New Carbonaceous Materials: The Role of Vibrational Spectroscopy. Carbon. **43**, 8 (2005) 1593-1609.

[15]   Naseh, M. V., Khodadadi, A. A., Mortazavi, Y., Sahraei, O. A., Pourfayaz, F., Sedghi, S. M., Functionalization of Carbon Nanotubes Using Nitric Acid Oxidation and DBD Plasma. Int J Chem Biol Eng. **37** (2009) 177–179.

[16]   Mohamad, I. S., Chitrambalam, S. T., Hamid, S. B. A., Chin, W. M., Yau, K. H., Febrian, I., A Comparison Study on the Heat Transfer Behavior of Aqueous Suspensions of Rod Shaped Carbon Nanotubes with Commercial Carbon Nanotubes. Advanced Materials Research. **667** (2013) 35-42.

[17]   Peigney, A., Laurent, C., Flahaut, E., Bacsa, R. R., Rousset, A., Specific Surface Area of Carbon Nanotubes and Bundles of Carbon Nanotubes. Carbon. **39**, 4 (2001) 507-514.

[18]   Agnihotri, S., Mota, J. P., Rostam-Abadi, M., Rood, M. J., Characterization of Single-Walled Carbon Nanotube Bundles by Experiment and Molecular Simulation. Langmuir. **21**, 3 (2005) 896-904.

[19]   Zelenka, T., Adsorption and Desorption of Nitrogen at 77 K on Micro- and Meso- Porous Materials: Study of Transport Kinetics. Microporous and Mesoporous Materials. **227** (2016) 202-209.

[20]   Endo, M., Hayashi, T., Kim, Y. A., Terrones, M., Dresselhaus, M. S., 2004. Applications of Carbon Nanotubes in The Twenty-First Century. Philosophical Transactions of the Royal Society of London A: Mathematical. Physical and Engineering Sciences. **362**, 1823 (2004) 2223-2238.

[21]   Mackie, E. B., Wolfson, R. A., Arnold, L. M., Lafdi, K., Migone, A. D., Adsorption Studies of Methane Films on Catalytic Carbon Nanotubes and on Carbon Filaments. Langmuir. **13**, 26 (1997) 7197-7201.

[22]   Zhu, W., Miser, D., Chan, W., Hajaligol, M., Characterization of Multiwalled Carbon Nanotubes Prepared by Carbon Arc Cathode Deposit. Materials Chemistry and Physics. **82**, 3 (2003) 638-647.

[23]   Li, F., Wang, Y., Wang, D., Wei, F., Characterization of Single-Wall Carbon Nanotubes by N_2 Adsorption. Carbon. **42**, 12, (2004) 2375-2383.

[24]   Kayiran, S. B., Lamari, F. D., Levesque, D., Adsorption Properties and Structural Characterization of Activated Carbons and Nanocarbons. The Journal of Physical Chemistry B. **108**, 39 (2004) 15211-15215.

[25] Raymundo-Pinero, E., Cazorla-Amorós, D., Linares-Solano, A., Delpeux, S., Frackowiak, E., Szostak, K., Béguin, F., High Surface Area Carbon Nanotubes Prepared by Chemical Activation. Carbon. **40**, 9 (2002) 1614-1617.