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NITRIC ACID TREATMENT OF EMPTY FRUIT BUNCH (EFB) –EFFECT THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF THE PRODUCT

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ABSTRACT

Self-adhesive carbon grains (SACG) were prepared from EFB by a low temperature pre-carbonization process. SACG are carbon powder that can be compacted into shape by a compression moulding technique without adding any binder. Green pellets were prepared from SACG and SACG treated with nitric acid (HNO_3) with different concentration. Carbon pellets were produced by carbonization of green pellets up to 1000°C in a nitrogen environment using a multi-steps heating profile. The mechanical properties such as hardness (*H)*, Young's modulus *(Y*), and microstructure of carbon pellets and commercial sample (Sigradur K) were determined using micro-hardness tester, UMC (Ultrasonic measurement with computer) system, and scanning electron microscope (SEM). The results show that the behavior of *H* and *Y* increased linearly with molarity. The behavior seems to be associated with the effect of acid treatment and was indicated on the samples microstructure.

INTRODUCTION

One of task of palm oil mills is to handle large amount of by-products such as empty fruit bunch (EFB), palm shells, pressed fruit fibers and palm oil mill effluent which are continuously generated during its operation. For example, the EFB requires large land area for temporary disposal and at the same time it may pollute the mill site if the storage time is too long. Effective utilization of the EFB and others by-product is expected to resolve or at least to minimize this problem and then will help the mills to operate productively. This solution is one of the crucial aspects in the context to ensure that Malaysia will maintain its position as a leading country in palm oil industry. In this context, there have been numerous attempts to maximize, for example the use of EFB, a by-product generated at palm oil mills, which amount to about 8.5 million metric tones annually [1]. The list of the EFB applications at commercial and research levels has been summarized elsewhere [2, 3]. Studies to develop the method that can use the EFB directly [4-7] or via the production of the self-adhesive carbon grains (SACG) from the EFB [8-10] for producing solid carbon products have been published elsewhere. Following these studies, a number of efforts have been made to improve the properties of carbon pellets from the SACG by optimizing the samples preparation parameters.

In the present study, the SACG were treated with nitric acid of different concentration. It should be noted that nitric acid has been widely used to treat carbon samples or precursor because it can form oxygen surface complex at the edge sites of carbon structures and hence effect the oxidation [11], structure [12], wetting, adsorption, electrical and catalytic properties of carbon samples [13]. Therefore, it was expected that carbon pellet prepared from the carbonization of green pellet from the acid (HNO_3) treated SACG would be different from that of the untreated SACG. In the case of treating the SACG using urea formaldehyde [14], acid (HCl) and alkaline (NaOH) [15] and iodine [16], a very apparent effect was observed. A similar effect was observed after optimization of milling time and particle size of the SACG [17], heating profile of the carbonization process [18] and concentration of acid (HNO_3) at a fixed reaction time [19].

MATERIAL AND METHOD

Summary of the EFB properties can be found elsewhere [2,3]. EFB is a natural polymer and its molecular compositions are 45-50% cellulose, 25-35% hemicellulose and 25-35% lignin.
The SACG were prepared from EFB fibers by a low temperature pre-carbonization process based on the method previously reported [8]. The pre-carbonized EFB was ball-milled for 40 h to obtain the SACG which can pass through a 53 microns sieve. SACG was treated with HNO_3 with four different concentration 1, 3, 5 and 7 Molar (*M*) at 100°C. These treated SACG was separated from the solution by a filtration process using filter papers (Whatman 41) and then dried in an oven at 105°C for 24 h. The treated SACG were ball-milled for 5 h and sieved to pass through a 53 microns sieve. The green pellets, designated as samples A, B, C, D and E were prepared by applying 21metric tonnes of compression force on 2 g of SACG and treated SACG respectively. These green pellets were carbonized up to 1000°C using a box furnace (Vulcan 3-1750) in order to obtain samples of carbon pellets. The furnace was set to operate using a multi-step heating profile [18, 20, 21]. The heating environment in the furnace was continuously filled with a flow of nitrogen gas at 1.0-1.5 liter per minute.
The dimension of the pellets before and after carbonization was measured using a micrometer and the density was determined by dividing the weight of the sample with its volume. The weight, dimension and density of the green pellets, and carbon pellets before and after being polished are shown in Table I. The hardness of carbon pellets was measured using a Shimadzu HMV 2000 micro-hardness tester. The load used in this measurement was 500 gf and the running time was 25 s. A pulse echo method was used to measure the velocity of longitudinal wave (*v)* across the carbon pellets. This was done by using the ultrasonic-measuring-computer (UMC) system that had a pulse echo method with MHz perspex delay time transducer and a sensitivity of 0.13 %. The signal from ultrasonic pulser (model Panametric 500PR)) was transferred to the computer via GPIB card for the calculation of longitudinal ultrasonic velocity in the sample. The formula of Young's modulus (*Y*) for the one-dimensional form of wave equation for the homogeneous and isotropic sample was used to calculate Y from v [7, 18]. The microstructure of the samples were recorded using the Scanning Electron Microscope (SEM: Phillip XL 30).

RESULTS AND DISCUSSION

Table I Weight (W), thickness (T), diameter (D), density (ρ), Vickers hardness (*H*) and Young's modulus (*Y* (GPa)) of the untreated samples (A), acid treated samples (B, C, D and E) and reference sample (F (Sigradur K)). *Data from supplier, $^{+}$ data after polished.

Sample	Before Carbonization				After Carbonization					
	W (g)	T (mm)	D (mm)	ρ (g/cm^3)	W (g)	T (mm)	D (mm)	ρ (g/cm^3)	*H*	*Y*
A(0M)	1.99	2.80	27.04	1.24	0.63^{+} 0.70	1.76^{+} 2.12	19.25	1.23^{+} 1.13	174	14
B(1M)	2.00	2.74	27.07	1.27	0.67^{+} 0.68	1.81^{+} 1.99	19.60	1.23^{+} 1.14	178	15
C(3M)	2.00	2.65	27.07	1.31	0.64^{+} 0.65	1.73^{+} 1.89	19.01	1.31^{+} 1.21	245	20
D(5M)	2.01	2.63	27.05	1.33	0.63^{+} 0.64	1.70^{+} 1.85	18.92	1.33^{+} 1.23	286	23
E(7M)	1.99	2.59	27.05	1.34	0.60^{+} 0.61	1.62^{+} 1.77	18.86	1.34^{+} 1.24	309	24
F	-	-	-	-	0.93	1.90	20.00	1.54	350 340*	34.9 35*

The data in Table I show that acid treatment causes a moderate increase in the density of the green pellets. It is possible that this has resulted from the property that the treated SACG is heavier in weight after chemisorp oxygen from nitric acid [14]. The data in Table I also show that after carbonization the density of carbon pellets (after polishing) B, C, D and E are slightly higher than that of sample A. This may be due to less porosity development which occurred in samples B, C, D and E during carbonization because acid has dissolved some of the volatile matters in the green pellets B, C, D and E.

The hardness (*H)* and Young's modulus (*Y*) of carbon pellets and commercial sample are also shown in Table I. As can be seen in this table, the value of *H* and *Y* appear to increase with the concentration (M) of HNO_3. These relationships can be approximately expressed in terms of the following linear equations.

H/[Vickers hardness] = 21.09 M + 170.93 (1)

Y/[GPa] = 1.41 M + 15.07 (2)

A similar linear relationship was observed on the electrical conductivity of carbon pellets against the increase of the percentage of heat-treated lignin from EFB and SACG from cotton cellulose added to the SACG from EFB used for green pellets preparation [4]. These results

seem to demonstrate that the property of carbon pellets from SACG from EFB can be easily modified by changing the property of the green pellets.

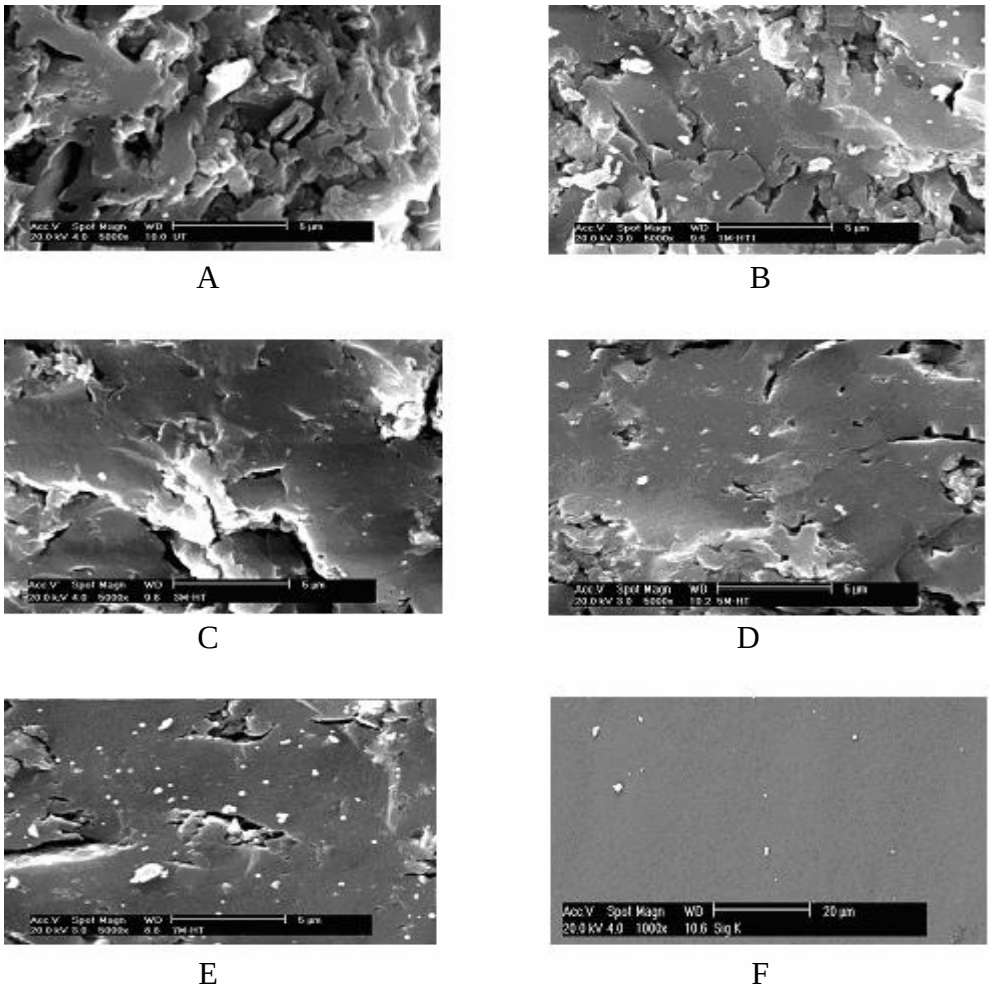

Figure 1 SEM micrographs of the untreated samples (A), acid treated samples (B, C, D and E) and reference sample (F (Sigradur K))

Before pre-carbonization, the role of lignin in EFB fibers is to bind the cellulose and hemicellulose to form a composite structure. Hemicellulose has partially decomposed due to pre-carbonization and lignin is no longer functioning as a cementing agent. The collapse of the composite structure makes the pre-carbonized EFB fibers brittle and therefore can be easily milled into powder form (SACG). Therefore, it is possible that an increase in acid concentration can expedite the breaking of the pre-carbonized EFB fibers into smaller particle size during milling process. Green pellets from carbon powder of smaller particle size allow the formation of a stronger inter-particles bonding during carbonization and hence result in a stronger and better microstructure of carbon pellets after carbonization. A similar formation of a stronger inter-particle bonding has been observed, for example, on carbon samples from phenolic resin [15]. This could be an explanation for the behavior that *H* and *Y* of the samples increase as the acid concentration increases.

It was found that there were noticeable differences between the SEM micrographs with the magnification of 5000X for samples A, B, C, D and E, indicating the effect of acid treatment on the samples microstructure (Figure 1). The microstructure and inter-bonding between

particles of the samples improved as a result of the acid treatment and the carbonization process. As expected, a remarkable difference can be observed between the SEM micrographs of these samples and the reference sample (F). These differences are consistent with the differences in their mechanical properties as shown in Table I.

CONCLUSION

The hardness (*H)* and Young's modulus (*Y*) of carbon pellets prepared from different concentration of nitric acid (HNO_3) treated self-adhesive carbon grains (SACG) were found to increase linearly with increasing concentration of acid. The *H* and *Y* of carbon pellet were found to be 9% and 34% respectively smaller than that of the commercial sample. This indicates that the change of SACG particle size, due to acid treatment systematically contributes toward the improvement of the property of the carbonized green pellets made from the acid treated SACG. It is possible that this is a general characteristic for carbon from lignocellulosic materials and if this is true, this linear relationship could be conveniently used for calibration purpose. However more data is needed to validate such a relationship, particularly for carbon samples from other type of lignocellulosic materials.

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REFERENCES

[1] Review of the Malaysian Palm Oil Industry (*Palm Oil Registration and Licencing Authority*[PORLA], Ministry of Primary Industry, Malaysia, 1997), (1996), 9.

[2] Mohamad Deraman, Sarani Zakaria, Mohamad Husin, Astimar Abdul Aziz, Ridzuan Ramli, Anis Mokhtar, Mohd. Nor Mohd. Yusof and Mohd. Hamami Sahri. X-ray Diffraction Studies on Fibers of Oil Palm Empty Fruit Bunch and Rubberwood for Medium Density Fiberboard. *J. Mater. Sci. Letters* (U.K./U.S.A.) 18(1999), 249-253.

[3] Sreekala M. S., Kumaran M. G. and Thomas S. Oil Palm Fibres: Morphology, Chemical Composition, Surface Modification and Mechanical Properties. *J. Appl. Polym. Sci*. 66(1997), 821-835.

[4] Mohamad Deraman. Resistivity of Carbon from Oil Palm Bunches: Percolation Theory. *J. Phys. D: Appl. Phys*. (United Kingdom) 27(1994), 1060-1062.

[5] Mohamad Deraman, Mohd. Pauzi Ismail and Ma'azam Md. Said. Young Modulus of Carbon from Mixture of Oil Palm Bunches and Latex. *J. Mater. Sci. Letters* (United Kingdom) 14(1995), 781-782.

[6] Mohamad Deraman and Mohd. Pauzi Ismail. Effect of Particle Size on the Young Modulus of Carbon from Oil Palm Bunches. *Pertanika J. Sci. & Tech.* (UPM) 3(2)(1995), 203-209.

[7] Mohamad Deraman, Ramli Omar, Ahmad Puaad Othman and Abd. Ghani Harun. Drying of Green Body of Solid Carbon Disc from Oil Palm Bunches: Diffusion Coefficient of Water Binder. *J. Solid State Sci. and Technol. Lett*. 5(1)(1998), 26-34.

[8] Mohamad Deraman, Ramli Omar and Abd. Ghani Harun. Young Modulus of Carbon from Self-adhesive Carbon Grain of Oil Palm Bunches. *J. Mater. Sci. Letters* (U.K./U.S.A.) 17(1998), 2059-2060.

[9] Mohamad Deraman and Ramli Omar. Thermal Conductivity of Carbon Pellets Prepared from Oil Palm Bunches. *Pertanika J. Sci. & Tech*. (UPM) 5(1)(1997), 1-13.

[10] Abdul Ghani Harun, Jamaludin Mohd. Daud, Mohamad Deraman dan Ramli Omar. Serbuk Karbon Swa-Merekat Daripada Serabut Tandan Kelapa Sawit: Analisis Spektrum Infra-Merah Transformasi Fourier. *J. Solid State Sci. and Technol. Lett*. 5(2)(1998), 98-107.

[11] Kyotani T., Nakazaki S., Wei-hua Xu, Tomita A. Chemical modification of inner walls of carbon nanotubes by HNO_3 oxidation. Carbon 39(2001), 771-785.

[12] Kamegawa K., Nishikubo K. and Yoshida H. Oxidative Degradation of carbon blacks with nitric acid (I)-changes in pore and crystallographic structures. Carbon 36(1997), 433-441.

[13] Otake Y. and Jenkins R. G. Characterization of Oxygen-Containing Surface Complexes Created on a Microporous Carbon by Air and Nitric Acid Treatment. Carbon 31(1993), 109-121.

[14] Mohamad Deraman, Marina Talib, Izan Roshawaty Mustapa, Ramli Omar, Sarani Zakaria, Mohamad Harun and Azhar Azmi. Hardness and Microstructure of Carbon Pellets from Mixtures of Urea Formaldehide and Self-adhesive Carbon Grain from Oil Palm Bunch. *J. Solid State Sci. and Technol. Lett.*, 7(1&2)(2000), 181-187.

[15] Mohamad Deraman, Marina Talib, Izan Roshawaty Mustapa, Ramli Omar, Sarani Zakaria, Azhar Azmi and Astimar Abdul Aziz. Hardness and Microstructure of Carbon Pellets from Acid and Alkaline Treated Self-Adhesive Pyropolymer Prepared from Oil Palm Bunch. *Proc. The Simposium Fisika Nasional XVIII, 25-27 April 2000,* Puspitek, Serpong, Indonesia, (2000), 483-491.

[16] Mohamad Deraman, Ramli Omar, Marina Talib, Izan Roshawaty Mustapa, Nor Hayati Alias, Sarani Zakaria and Rosly Jaafar. Electrical and Mechanical Properties of Carbon Pellets From Iodine Treated Self-Adhesive Carbon Grain From Oil Palm Empty Fruit Bunch. *J. Solid State Sci. and Technol. Lett.*, 8(1&2)(2000), 77-82.

[17] Mohamad Deraman, Marina Talib, Izan Roshawaty Mustapa, Ramli Omar, Sarani Zakaria, Rosli Jaafar and Mohd Nor Mohd Yusuff. Effects of Milling Time on Properties of Carbon Pellets from Oil Palm Empty Fruit Bunch. *Proc. The Fifth National Sem. on Utilization of Oil Palm Tree (Oil Palm Biomass: Opportunities and Challenges in Commercial Exploitation),* ed. Wan Asma Ibrahim et al. (OPUTC(Oil Palm Tree Utilization Committee)), (2000), 211-218.

[18] Azhar Azmi and Mohamad Deraman. Kajian Awal Penyediaan dan Pencirian Produk Karbon Dari Papan-Zarah Teracuan Berasaskan Tandan Kelapa sawit. *Proc. Postgraduate Colloquium, Faculty of Applied and Physical Sciences, Univ. Kebangsaan Malaysia,* ed. Mohd. Yusof Hj. Othman (FSFG, UKM), (1998), 240–245.

[19] Mohamad Deraman, Izan Roshawaty Mustafa, Ramli Omar, Marina Talib, Sarani Zakaria and Nor Hayati Alias. Mechanical and Electrical Properties of Carbon Pellets Prepared From HNO_3 Treated Self-Adhesive Carbon Grain From Oil Palm Empty Fruit Bunch. Summitted to *J. Mater. Sci.*

[20] Byrne C. E. and Nagle D. C. Carbonization of Wood for Advanced Materials Application. *Carbon* 35(2)(1997), 259-266.
[21] Byrne C. E. and Nagle D. C. Carbonized Wood Monoliths-Characterization. *Carbon* 35(2)(1997), 267-273.