JOURNAL OF MATERIALS SCIENCE **37** (2002) 3329–3335

Electrical and mechanical properties of carbon pellets from acid (HNO_3) treated self-adhesive carbon grain from oil palm empty fruit bunch

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Factors such as its natural properties, low cost and availability in large quantities as a by-product may give oil palm empty fruit bunches (EFB) a great potential as a candidate precursor for solid carbon products. Self-adhesive carbon grains (SACG) were prepared from EFB by a low temperature pre-carbonization process. Green pellets were prepared from SACG and SACG treated with nitric acid having concentration of 1, 3 and 5 Molar (M). Carbon pellets were produced by carbonization of green pellets up to 1000°C in a nitrogen environment using multi-step heating profile. Measurements on carbon pellets show that the electrical conductivity (σ), hardness (H) and Young's modulus (Y) follow the linear equations $\sigma/[10^{-3} \times (\mu\text{m } \Omega)^{-1}] = 0.57M + 4.74$, $H/[\text{Vickers hardness}] = 27M + 148$ and $Y/[\text{GPa}] = 2.6M + 5.0$, respectively. This indicates that nitric acid systematically affected the properties of the product. The behavior that σ, H and Y increase linearly with M seems to be associated with the effect of acid treatment on the weight loss, lignocellulosic structure and particle size of the SACG.

1. Introduction

Oil palm empty fruit bunch (EFB) has traditionally been used as boiler fuel, mulching material in the oil palm plantation and organic fertilizer (after burning). However, numerous efforts have been made to widen its usage as a starting material for making different types of products including chemically modified fibre [1, 2], fiberboard [3] and solid carbon [4–12]. If solid carbon can be manufactured from EFB, this will help reduce Malaysian import since the yearly average of import over the last five years amounted to about RM120 million [12]. Since the supply of EFB is continuous at palm oil mills and annual production of EFB approximately amounted to 8.5 million tones, this material is considered to have a great potential for commercial exploitation [13].

EFB was found suitable to be converted, by a pre-carbonization process, into self-adhesive carbon grains (SACG) that can be pelletised without using any binding agent [7]. A number of attempts have been made in order to further improve the property of solid carbon product prepared from SACG [4–6]. In the present study, SACG was treated with nitric acid of different concentrations before it was pelletised into green pellets and then carbonised into carbon pellets. The objective of this study is to observe the relationship between the electrical conductivity, hardness and Young modulus of the carbon pellets with the concentration of nitric acid used to treat the SACG. For other materials such as carbonised phenol-formaldehyde resin, the treatment using nitric acid was found to be effective in changing the characteristic of the final products since nitric acid causes the formation of oxygen surface complex at the edge sites of carbon structures [14]. The nature of this complex can influence the wetting, adsorption, electrical and catalytic properties of a carbon sample. Information from X-ray diffraction (XRD) and thermogravimetric analysis (TGA) results were used to discuss the effect of acid treatment on the properties of SACG and carbon pellets produced from the treated SACG. The results obtained were also compared with that of the reference sample (Sigradur K).

2. Material and method

Some of the properties of EFB have been summarized elsewhere [11]. EFB are stringy and flexible, and consist of fibres or bundles of fibres. The composition of fresh EFB are 34% dry matter, 3% oil and 63% water, and represents about 20 to 22% of the weight of fresh fruit bunches. EFB is a natural polymer; a lignocellulosic material containing 45–50% cellulose, 25–35% hemicellulose and 25–35% lignin. In the dry form, the mean percentages of chemical composition are: ash

TABLE I Mass (W), thickness (T), diameter (D), density (ρ), electrical conductivity ($\sigma \times 10^{-3}$ (μm Ω)$^{-1}$), Vickers hardness (H) and Young's modulus (Y (GPa)) of the untreated samples (A), acid treated samples (B, C and D) and reference sample (E (Sigradur K)).

	Before carbonization				After carbonization						
Sample	W (g)	T (mm)	D (mm)	ρ (kg/m^3)	W (g)	T (mm)	D (mm)	ρ (kg/m^3)	σ	H	Y
A(0M)	2.01	2.70	27.04	1250	0.76 0.64[a]	2.16 1.70[a]	19.35	1180 1280[a]	5.38	180	8
B(1M)	1.99	2.70	27.03	1290	0.72 0.66[a]	1.96 1.66[a]	19.69	1230 1340[a]	5.71	195	10
C(3M)	1.97	2.57	27.03	1340	0.62 0.58[a]	1.72 1.46[a]	19.17	1270 1360[a]	6.62	225	12
D(5M)	1.94	2.45	27.02	1370	0.60 0.58[a]	1.65 1.49[a]	18.66	1340 1420[a]	6.99	260	16
E	–	–	–	–	0.93	1.90	20.01	1540	18.20 20.00[b]	350 340[b]	34.9 35.0[b]

[a]Data after polished.
[b]Data from supplier.

(6.3), oil (8.9), C (42.8), N_2(0.8), P_2O_5(0.22), K_2O (2.9), MgO (0.3) and CaO (0.25).

EFB fibers were pre-carbonized at low temperature based on the method previously reported [7]. The pre-carbonized EFB was ball-milled for 20 h to obtain self-adhesive carbon grains (SACG) with particle sizes that can pass through 53 microns sieve. SACG was treated with nitric acid (HNO_3) with three different concentrations 1, 3 and 5 Molar (M). For each concentration, 15 g of SACG was mixed with 2.0×10^{-4} m^3 of HNO_3 and stirred by a magnetic stirrer for 1 h at room temperature. The treated SACG was left for 16 h, before it was separated from the solution by a filtration process using filter papers (Whatman 41). The treated SACG was then dried in an oven at 60°C for a few hours. The green pellets, designated as samples A, B, C and D, were prepared by applying 20 metric tonnes of compression force on 2 g on SACG, and on SACG treated with 1, 3 and 5M of HNO_3 respectively in a mould of 25 mm diameter. In order to obtain samples of carbon pellets, these green pellets were carbonized up to 1000°C using a furnace equipped with a heating rate controller facility (Vulcan Box Furnace 3-1750). The heating environment in the furnace was continuously filled with nitrogen gas whose flow rate was 1.0–1.5 $\times$ 10^{-3} m^3/min. The profile of the multi-step heating program used was based on the requirement previously proposed [15–17].

The dimensions of the pellets before and after carbonization were 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.

X-ray diffraction measurements on SACG were conducted using a Siemens (D5000) diffractometer which employed Cu K (0.1542 nm) radiation. Shimadzu Thermal Analyzer 501 was used to obtain the thermograms of the SACG in the temperature range up to 600°C in an inert atmosphere at the heating rate of 20°C/min.

Electrical resistivity of the carbon pellets was measured using the four-point-probe technique (Keithley Micro-Ohmmeter). The hardness of carbon pellets was measured using a Shimadzu HMV 2000 microhardness tester. The load used in this measurement was 4.9 N 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 the 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 the wave equation for the homogeneous and isotropic sample was used to calculate Y from v [7, 18]. The microstructures of the samples were recorded using the Scanning Electron Microscope (SEM: Phillip XL 30).

3. Results and discussion

Fig. 1 shows the X-ray diffractograms for the EFB and SACG (A, B, C and D) samples. The general feature

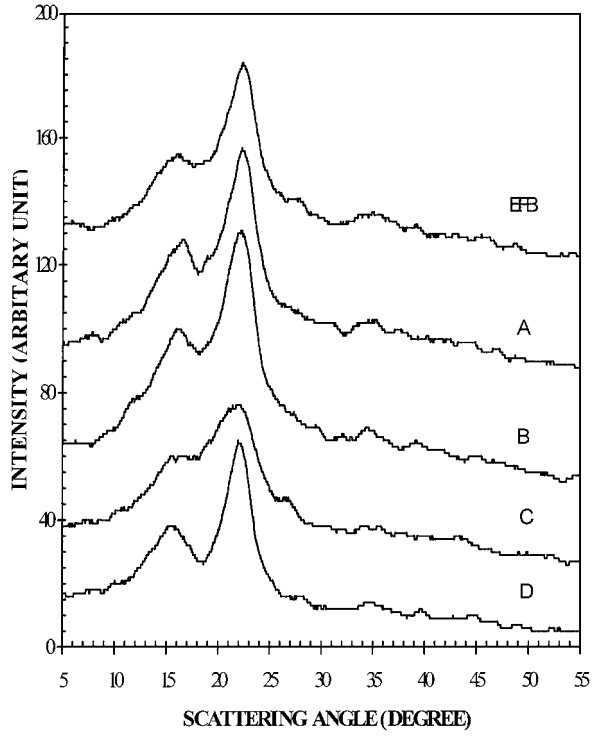


Figure 1 X-ray diffraction profiles of the samples EFB, A, B, C and D.

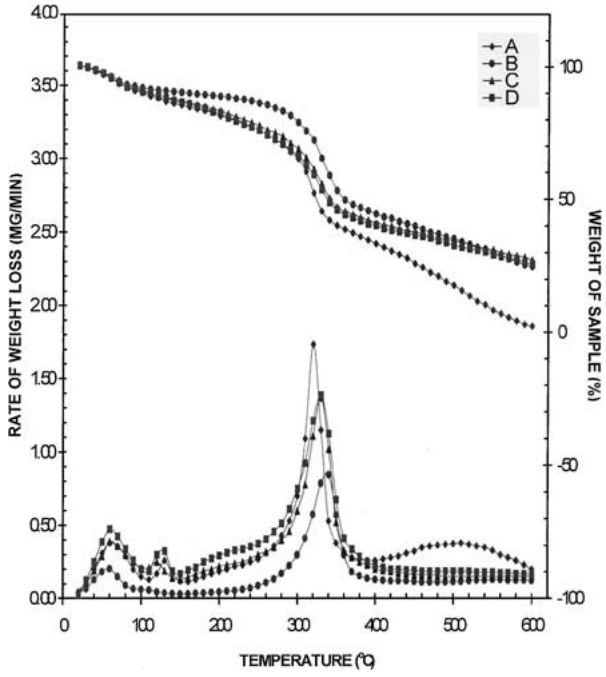


Figure 2 TGA-DTA profiles of the samples A, B, C and D.

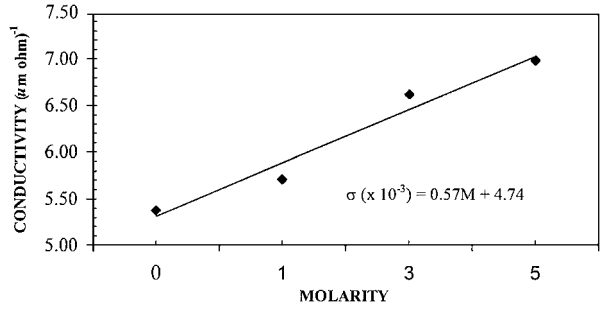


Figure 3 Electrical conductivity as a function of nitric acid concentration for the samples A, B, C and D.

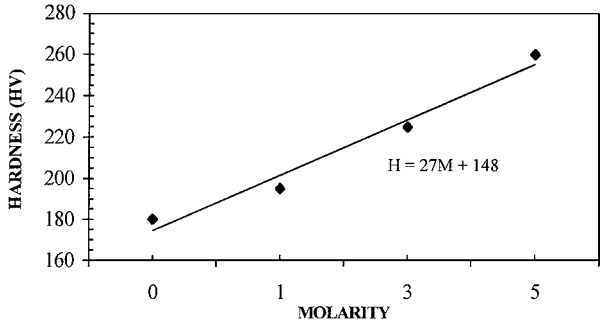


Figure 4 Vickers hardness as a function of nitric acid concentration for the samples A, B, C and D.

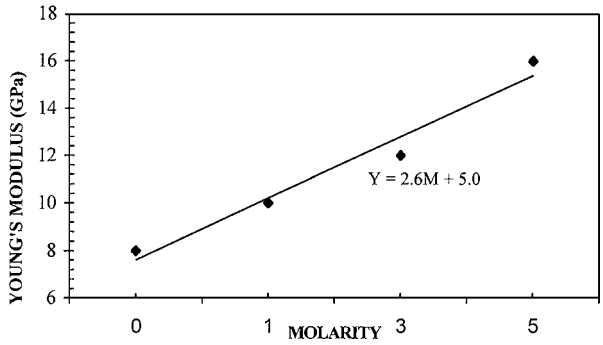


Figure 5 Young's modulus as a function of nitric acid concentration for the samples A, B, C and D.

of the cellulose diffraction peak for the SACG (treated and untreated) samples, particularly the 002-peak at 2θ about 22.6°, and the composite of 101- and $10\bar{1}$-peaks at 2θ about 15.4°, looks very similar with that of the EFB sample. This shows that the lignocellulosic structure of the samples does not collapse during the pre-carbonisation process up to the temperature of 280°C. The peak resolution between the 002-peak and the composite peaks of 101 and $10\bar{1}$ becomes better after acid treatment; these two peaks for the treated SACG are sharper than that of the untreated SACG. It is possible that the component which contributes to the peak broadening has already dissolved or underwent structural change during nitric acid treatment. Such a component is possibly a decomposed hemicellulose resulted during pre-carbonisation since cellulose and lignin in lignocellulosic materials decompose at temperatures higher than 280°C [15].

Analysis of the TGA results for the temperature range from 20°C to 600°C shows that the acid treated SACG gives a higher carbon yield compared to that of the untreated SACG. Fig. 2 shows that the increase in acid concentration causes the main peak height and position of the rate of weight lost to decrease and slightly shift to the higher temperature region respectively. This indicates that the acid treatment has changed the thermal property of the SACG.

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 chemisorbing oxygen from nitric acid [14]. The data in Table I also show that after carbonisation the density of carbon pellets (after polishing) B, C and D are slightly higher than that of sample A. This may be due to less porosity development which occurred in samples B, C and D during carbonization because acid has dissolved some of the volatile matter in the green pellets B, C and D. Such a reduction of volatile matter is indirectly indicated in the TGA data in Fig. 2, which shows that carbon yield is higher for the treated SACG than the untreated SACG.

The electrical conductivity, hardness and Young's modulus of carbon pellets and commercial sample are shown in Table I. As can be seen in this table, the value of electrical conductivity (σ), hardness (H) and Young's modulus (Y) appear to increase with the concentration of nitric acid. The plot in Figs. 3, 4 and 5, based on the data in Table I, shows that the σ, H and Y increase linearly with the acid concentration (M) used for the treatment of SACG. These relationships can be approximately expressed in terms of the following linear equations

$$\sigma/[10^{-3}\mathrm{x}(\mu\mathrm{m}\ \Omega)^{-1}] = 0.57M + 4.74 \quad (1)$$

$$H/[\text{Vickers hardness}] = 27M + 148 \quad (2)$$

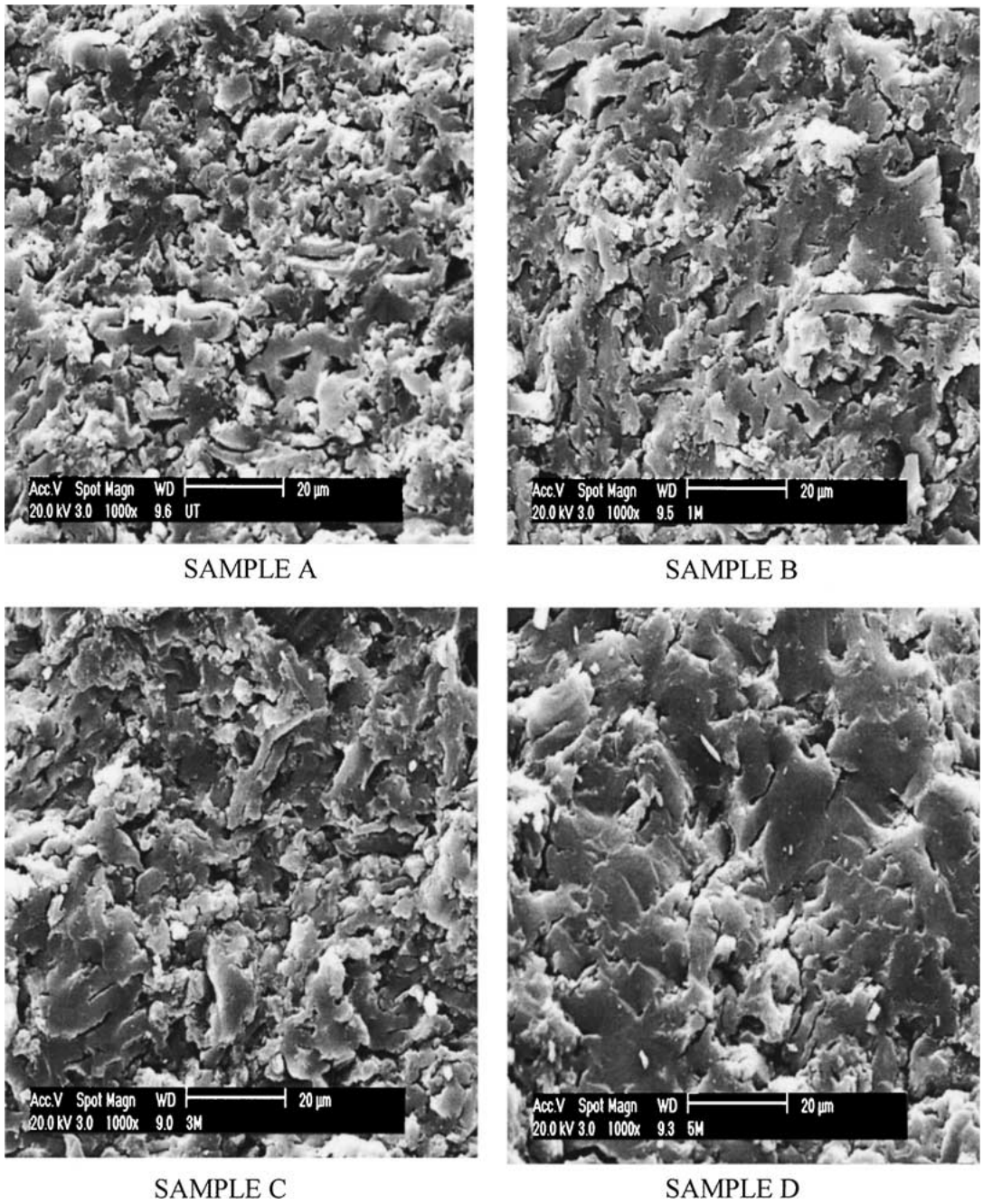
$$Y/[\mathrm{GPa}] = 2.6M + 5.0 \quad (3)$$

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.

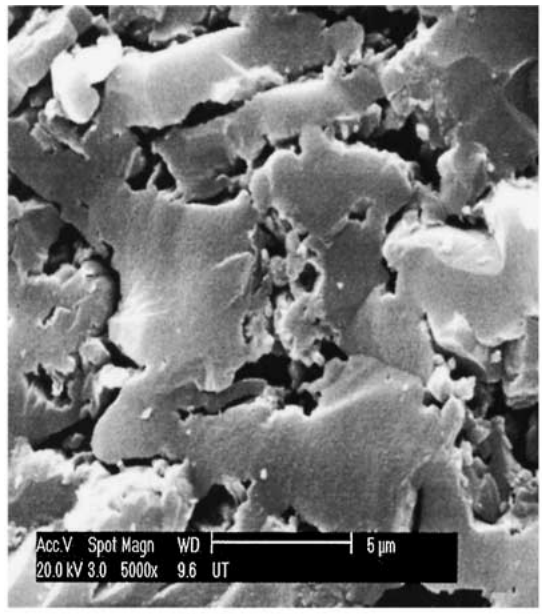
Before pre-carbonization, the role of lignin in EFB fibers is to bind the cellulose and hemicellulose to form a composite structure. Hemicellulose has partially decomposed due to pre-carbonization and lignin is no longer functioning as a cementing agent. The collapse of the composite structure makes the pre-carbonized EFB fibers brittle and therefore they can be easily milled into powder form (SACG). However, as shown by the X-ray diffraction profile in Fig. 1, EFB retains its lignocellulosic structural system after pre-carbonization. Mechanical properties of this system can be weakened by acid or alkali treatment [19]. 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 the milling process. Green pellets from carbon powder of smaller particle size allow the formation of stronger inter-particle 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 [20]. This could be an explanation for the behavior that electrical conductivity (σ), hardness (H) and Young's modulus (Y) of the samples increase as the acid concentration increases.

It was found that there were noticeable differences between the SEM micrographs with magnifications of 1000X and 5000X for samples A, B, C and D, indicating the effect of acid treatment on the samples microstructure (Fig. 6). As expected, a remarkable difference can be observed between the SEM micrographs of

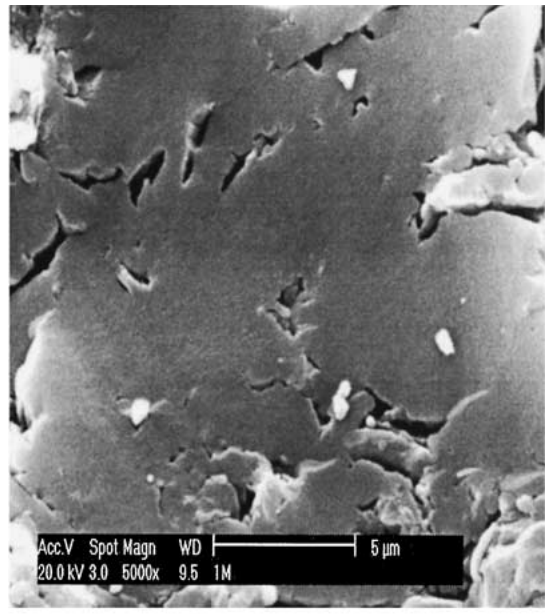


(a)

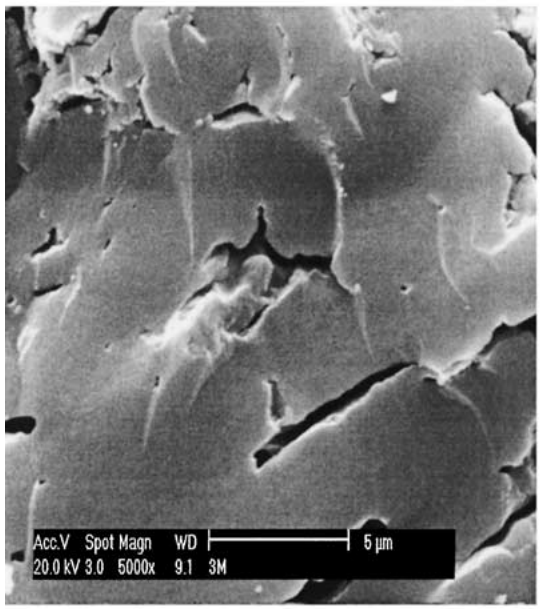
Figure 6 SEM micrographs of the samples A, B, C, D, and Sig K: (a) 1000×, (b) 5000×, (c) 1000× and (d)5000×. (*Continued.*)



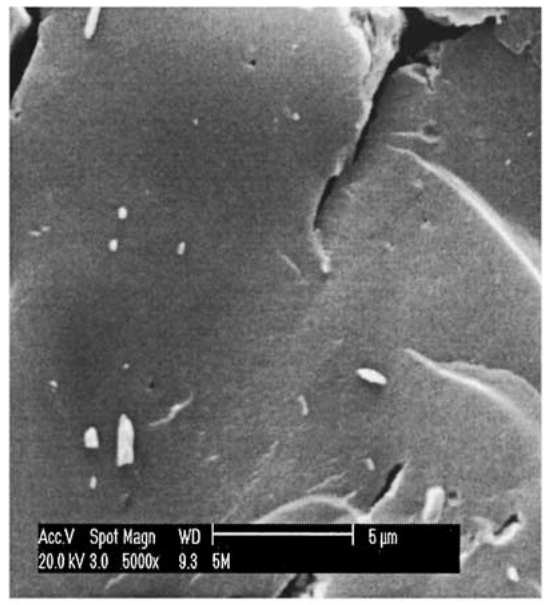
SAMPLE A



SAMPLE B

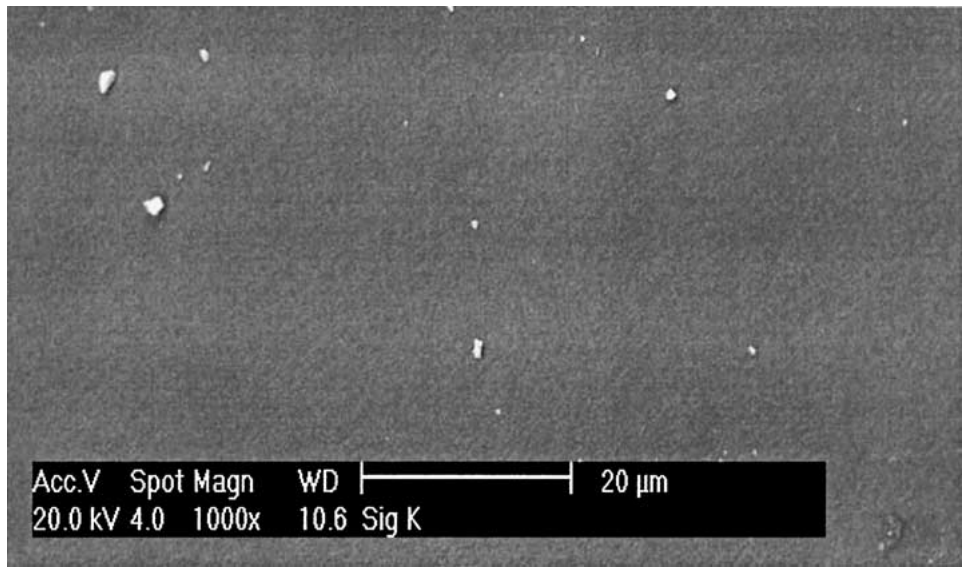


SAMPLE C



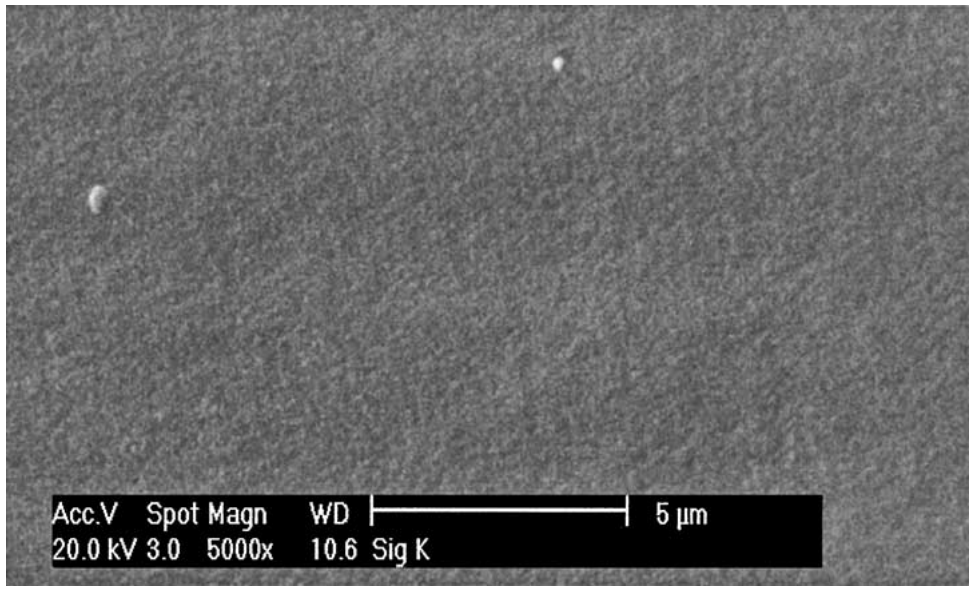
SAMPLE D

(b)



(c)

Figure 6 (*Continued.*)



(d)

Figure 6 (*Continued.*)

these samples and the reference (Sig K) sample (Fig. 6). These differences are consistent with the differences in their mechanical and electrical properties as shown in Table I.

Our X-ray diffraction data on carbon pellets from EFB produced by carbonization up to 1000°C has shown that the sample has a turbostratic structure [21]. In general such a structure is exhibited by carbon samples from lignocellulosic materials [22]. It is expected that such a structure would be exhibited by carbon pellets A, B, C and D. Therefore, no attempt was made to conduct X-ray diffraction measurements on these samples.

4. Conclusions

Self-adhesive carbon grains (SACG) prepared from fibres of oil palm empty fruit bunch were treated with nitric acid having different concentrations. Electrical conductivity, hardness and Young modulus of carbon pellets prepared from the acid treated SACG were found to increase linearly with increasing concentration of acid. This indicates that the change of SACG particle size, weight lost as revealed by the TGA, and lignocellulosic structure as revealed by the XRD data, 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 are needed to validate such a relationship, particularly for carbon samples from other types of lignocellulosic materials.

Acknowledgements

Intensification of Research Priority Area (IRPA) grant (Code 09-02-02-0070/ 09-02-02-0022-EA077) from Ministry of Science, Technology and Environment for the project entitles "Advanced Carbon Product from Oil Palm Bunches", Prof. Dr. Khalijah bte Mohd Salleh and the assistance of Mr. S. Sain, Mr. Z. M. Yusof and Mr. R. Datau are gratefully acknowledged.

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Received 14 February
and accepted 15 March 2002