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Full Length Research Paper

Nanocarbonfibril in rice flour charcoal

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This paper presents the results of a study of nanocarbonfibrils in charcoals, which were prepared from rice flour with diameters of 90, 75 and 38 µm, respectively. The rice flours were carbonized for 30 min at a temperature of 600 to 800°C. The carbonized products were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectrometer (FTIR), energy dispersive X-ray spectrometer (EDS) and X-ray diffractometer (XRD). Nanocarbonfibrils with diameters of 59.42 to 68.38 nm were found in all carbonized products. The other nanocarbons exhibited by the products are carbon granules with diameters ranging from 0.9 to 1.1 µm. The most functional groups on surface charcoals are OH-stretching, C=C stretching, P-O-C stretching and Si-O-C stretching. The charcoal products are composed of amorphous carbon together with SiO_2, K_2CO_3, K_2O, KO_2, Mg and P.

Key words: Rice flour charcoal, nanocarbonfibril, nanostructure carbon, carbonization.

INTRODUCTION

Starch granules are composed of two types of *alpha*-glucan, amylose and amylopectin. Cereal starches contain integral lipids in the form of lysophospholipids and free fatty acids. Purified starches contain <0.6% protein and small quantities (<0.4%) of such minerals (as calcium, magnesium, phosphorus, potassium and sodium) (Tester et al., 2004). Starch structures consist of granule (2 to 100 µm), growth ring (120 to 500 nm), blocklet (20 to 500 nm), amorphous and crystalline lamellae (9 nm) and amylopectin and amylase chain levels (0.1 to 1.0 nm), according to Vandeputte and Delcour (2004). Carbon spheres have been synthesized from corn starch by a two stage process (oxidation and carbonization) after which the products kept the original shape of corn starch perfectly and the diameters of carbon spheres ranged from 5 to 25 µm (Zhao et al., 2008). The activated carbon spheres, that were prepared from potato starch by carbonization followed by activation with KOH, were hollow and retained the original morphology of potato starch with a decrease in size (Zhoa et al., 2009). Xue et al. (2004) prepared a carbon atom wire by pyrolysis of starch. The carbon atom wire is composed of winding lines with a diameter of around 20 nm. Moreover, activated carbons prepared from cationic starch using KOH, $ZnCl_2$ and $ZnCl_2/CO_2$ activation were used for the electrodes of a supercapacitor. The supercapacitor exhibited excellent capacitance characteristics in 30 wt% KOH aqueous electrolytes and showed a high specific capacitance of 238 F/g at 370 mA/g, which was nearly twice that of the commercial activated carbon (Wang et al., 2008). Additionally, the reinforcing potentials of cellulose nanofibers obtained from a starch-based thermoplastic polymer have been found to show diameters in the range of 10 to 80 nm and lengths of several thousand nanometers (Alemdar and Sain, 2008). Carbon fibers are sought for many applications, e.g. supercapacitor electrodes (Wang et al., 2008), reinforcement (Alemdar and Sain, 2008), ultraviolet (UV) absorbents (Ma et al., 2009) and hydrogen storage (Shindo et al., 2004).

In this research, the nanocarbonfibrils in rice flour charcoal were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectrometer (FTIR), energy dispersive X-ray spectrometer (EDS) and X-ray diffractometer (XRD). The effects of sizes of rice flour and carbonization temperature to nanocarbon in charcoals were studied.

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Table 1. Percent yield of rice flour charcoals from different sizes of fresh rice flour and carbonized temperature.

Charcoals from	Percent yield of rice flour charcoals carbonized at		
	600°C	700°C	800°C
90 µm rice flour	22.27	21.78	20.12
75 µm rice flour	18.92	18.50	17.03
38 µm rice flour	17.01	16.90	16.17

MATERIALS AND METHODS

Dried Zhao flour starch powders (obtain from Phitsanulok market, Thailand) were sieved to sizes of 170 mesh (90 µm), 200 mesh (75 µm) and 400 mesh (38 µm). The starch powders of each size were carbonized at 600, 700 and 800°C in electric furnace (Fisher Scientific Isotemp® Muffle Furnace). The temperature was increased with a rate of 15°C/min up to the desired temperature and was kept constant for 30 min. At last, the powders were cooled to room temperature. The carbonized products were analyzed for percent yield and were characterized by a Fourier transform infrared spectrometer (FTIR, Spectrum GX, Perkin Elmer), scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDS, LEO 1455 VP), transmission electron microscope (TEM, Phillips, Tecnai12) and X-ray diffractometer (XRD, PW 3040/60, X' Pert Pro MPD).

RESULTS AND DISCUSSION

Percent yield of charcoals

The results of percent yield of rice flour charcoals carbonized at 600 to 800°C are shown in Table 1. They reveal that the percent yield of charcoal decreases as the carbonized temperature increases and the size of rice flour decreases. The increase of the carbonization temperature leads to a higher thermal degradation, resulting in a decreasing percent yield of charcoal (Trompowsky et al., 2005). The percent yield of rice flour charcoals is size-dependent, e.g. gradually decreasing from 22.27% in the 90 µm fraction to 17.01% in the 38 µm one for carbonization at 600°C. An explanation for this behavior is that the smaller sizes of rice flours have a higher surface area which progressively oxidizes and that they probably exhibit a more branched structure created by the small grains (Francioso et al., 2011).

FTIR spectroscopy

The FTIR spectra of fresh rice flour and rice flour charcoals with carbonization at 600°C are shown in Figure 1. This figure shows the effect of starch powder size on carbonization. The broad band of fresh rice flour (sample) at 3400 cm^{-1} represents the –OH stretching vibration, possibly including H_2O, alcoholic OH, phenolic OH and/or carboxylic OH (Ascough et al., 2011), and the peaks at 2931 cm^{-1} are due to stretching vibrations of aliphatic CH (Guo and Bustin, 1998). The peak of OH is narrower after carbonization (Figure 1A to C), which suggests an increase in the number of oscillation modes that could be attributed to the presence of new hydrogen bonding interactions (Liu et al., 2011). The peak at 2931 cm^{-1} almost disappeared in the carbonized products, indicating that the hydrogen element was removed to a large extent (Wang et al., 2011). The peak at about 1700 cm^{-1} (C=O stretching band) in fresh powder starch is attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic and *p*-coumeric acids of hemicelluloses (Alemdar and Sain, 2008). This peak disappears completely in the starch powder charcoals, suggesting a destruction of these groups during the carbonization process. The peak between 1600 and 1500 cm^{-1} can be attributed to aromatic C=C ring stretching (Guo and Bustin, 1998). The absorption at 1300 to 900 cm^{-1} could be tentatively ascribed to the phosphorus species. These peaks may be assigned to ionized linkage P–O in acid phosphate esters (Puziy et al., 2002) or in form of phosphate ester groups (Pérez et al., 2005). The absorption in this region is also characteristic for silicon compounds and silicates, which is ascribed to the Si–C or Si-O fundamental stretching vibration (Qian et al., 2004). These peaks are still present in charcoals, suggesting the contribution of phosphorus compounds and silicon compounds in rice flour charcoals. The bands region located from 1200 to 1000 cm^{-1}, which is often considered as the vibration modes of C–C and C–O stretching and the bending mode of C–H bonds or the stretching vibration of C-O bond in C-O-H and C-O-C group, were attributed to saccharide (Liu et al., 2011) or the anhydrous glucose ring (Chen et al., 2008). The band due to aliphatic C–O–C and alcohol–OH in the range of 1060 to 1030 cm^{-1} in the spectrum of fresh rice flour, which represents oxygenated functional groups of cellulose (Guo and Bustin, 1998), is completely eliminated after carbonization. The FTIR spectra of all charcoals from rice flour powder with different sizes are the same (Figure 1A to C), thus indicating that the size of rice flour does not affect the behavior degradation of surface groups on starch powder.

Figure 2 shows the effect of carbonization temperature (600 to 800°C) on the FTIR spectra of rice flour charcoals. The FTIR spectrum of rice flour charcoal formed at 600°C shows similar characteristics to that

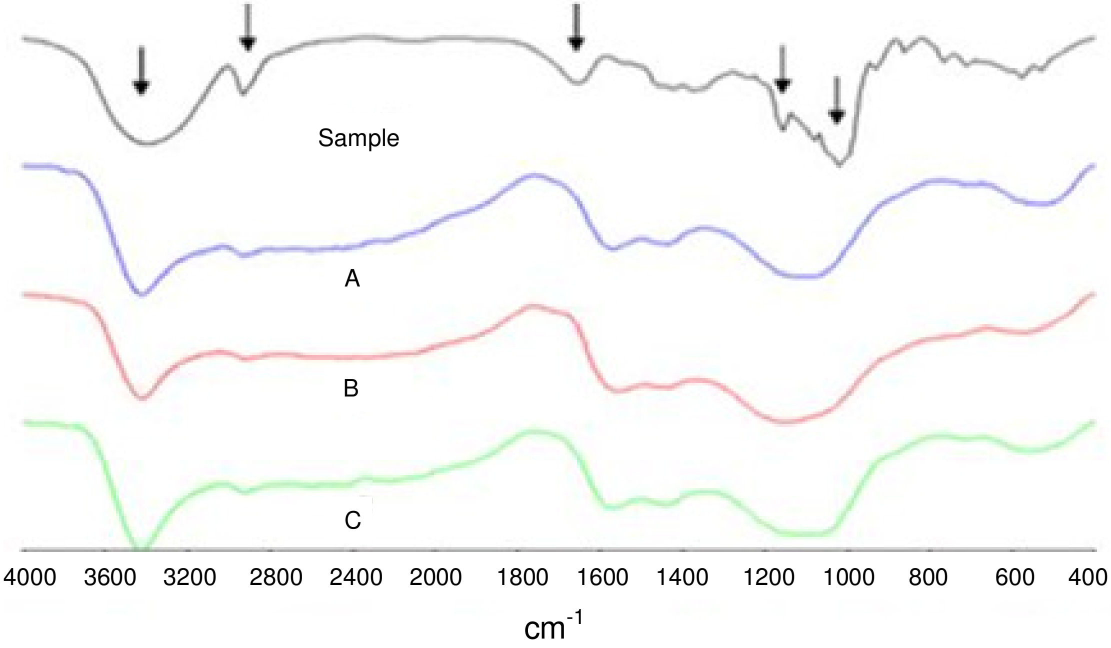

Figure 1 FTIR transmission spectra of charcoals produced from rice flour powder by carbonization at 600℃: sample = fresh rice flour, A = 90 µm rice flour charcoal, B = 75 µm rice flour charcoal, C = 38 µm rice flour charcoal.

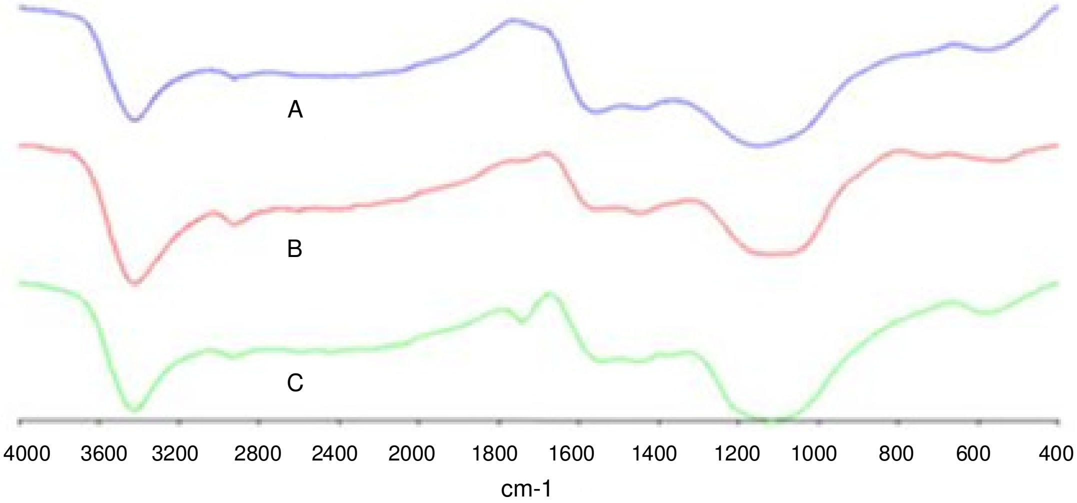

Figure 2. FTIR transmission spectrum of 75 µm charcoals produced from rice flour by carbonization at 600 to 800℃: A = rice flour charcoal at 800℃, B = rice flour charcoal at 700℃ and C = rice flour charcoal at 600℃.

formed at 700 and 800℃, but those of acid C=O groups (at about 1750 cm^{-1}) of rice flour charcoal formed at 600℃ recede at higher carbonization temperatures. This phenomenon probably originates from rearrangement and cyclization reactions of organic matter at high temperatures, where it vanishes completely after carbonization above 700℃.

SEM micrographs

The SEM micrograph of fresh rice flour is as shown in Figure 3a. The starch granules were polygonal with sharp angles and edges. The granule sizes are 3 to 6 µm in diameter. A selection of SEM micrographs of the charcoal surfaces is as shown in Figure 3b to f. It clearly shows

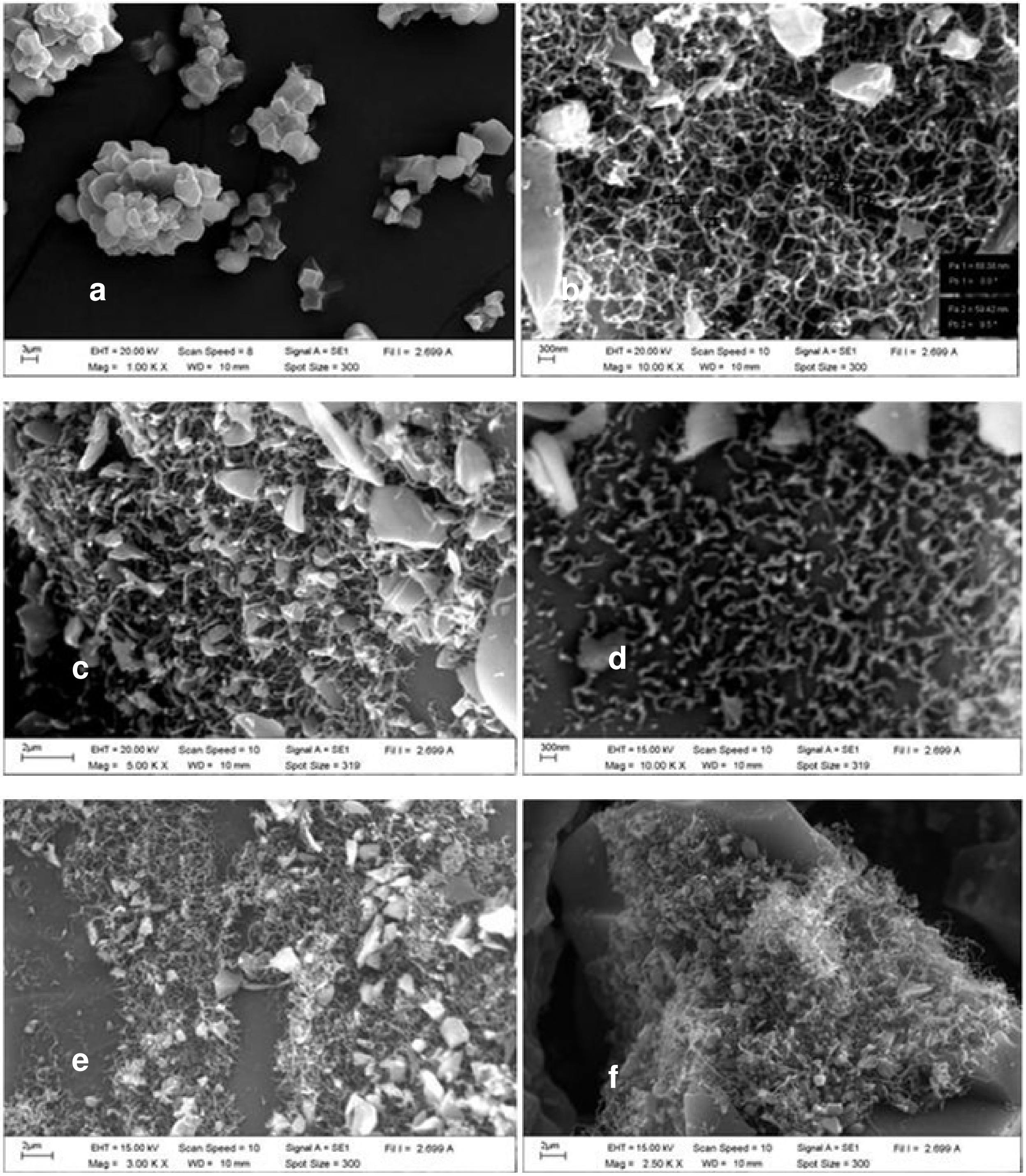

Figure 3. SEM micrographs of (a) fresh rice flour, (b) 90 µm rice flour charcoal carbonized at 600℃, (c) 38 µm rice flour charcoal carbonized at 600℃, (d) 38 µm rice flour charcoal carbonized at 700℃, (e) 90 µm rice flour charcoal carbonized at 800℃, (f) 38 µm rice flour charcoal carbonized at 800℃.

the shape and size distribution of the agglomerate nanocarbonfibrils and some carbon granules existed outside of the charcoal surfaces, even at different carbonized temperatures (Figure 3c, d and f) and starch powder sizes (Figure 3b, c, e and f). The SEM images of charcoals show that the surface texture of the sample consisted of uniformly distributed nanocarbonfibrils. The nanocarbonfibrils morphology looks like microfibrillated cellulose (Ray and Bousmina, 2005) with diameters of 59. 42 to 68.38 nm and high length (micrometer scale).

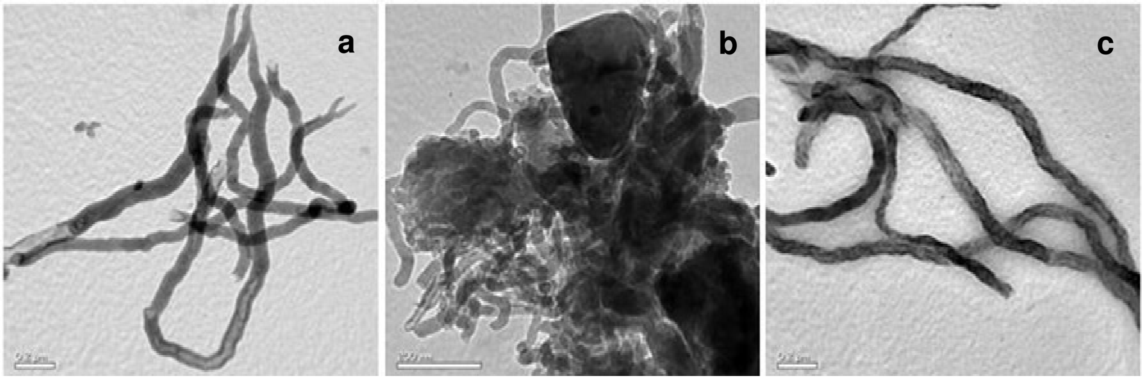

Figure 4. TEM photographs of (a and b) 90 µm rice flour charcoal carbonized at 600°C, (c) 90 µm rice flour charcoal carbonized at 700°C.

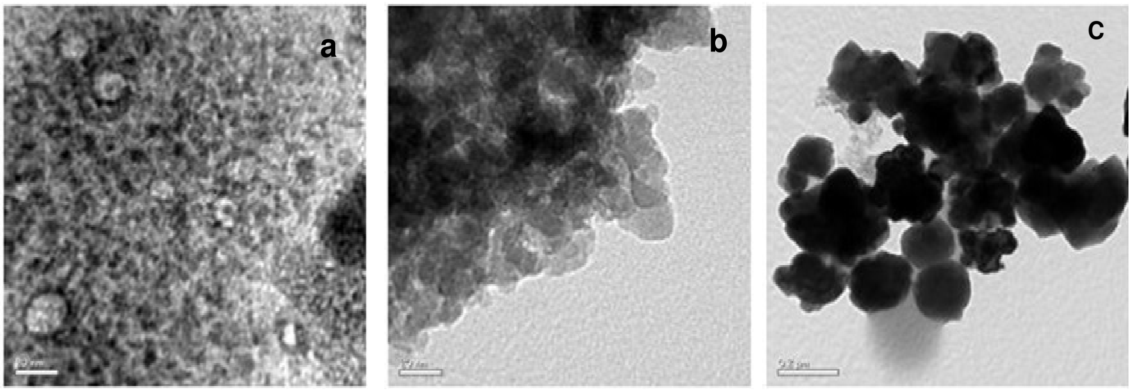

Figure 5. TEM photographs of (a and b) 75 µm rice flour charcoal carbonized at 600°C, (c) 75 µm rice flour charcoal carbonized at 700°C.

The nanocarbonfibrils were formed from the cellulose nanofibrils content of original starch. The size of carbon granules are 0.9 to 1.1 µm with smaller size than that of fresh granules.

TEM micrographs

The particular structures of the nanocarbonfibrils observed by TEM are shown in Figure 4. It can be seen that the nanocarbonfibrils are shaped like a snake and warp with nanosizes. Diameter and length of the nanocarbonfibrils were found to be in the range of 75 to 120 nm and 1.5 to 3.5 µm, respectively. A tendency to agglomeration was also observed from the TEM data (Figure 4b) in association with SEM data.

The other structures of charcoal particles are quasispherical and polygonal in shape with a diameter of 0.05 to 2 µm (Figure 5c). Further TEM examination at high magnification (Figure 5a and b) revealed that the carbon has a typical cryo-fractured surface.

EDS spectrum

Figure 6 shows the EDS spectrum from the rice flour charcoal carbonized at 600°C. From the spectrum, C is seen to be the main element (77.06 wt%), whereas O (16.81 wt%), Si (1.05 wt%), P (3.77 wt%) and K (1.30 wt%) are of secondary importance. The charcoal shows slightly high carbon content, indicating an increase in the amount of polycondensed aromatic structures which reflects the progressive aromatization of the original materials. Zhang et al. (2002) explained that above 400°C, the starch structure is destroyed and the product appears structurally similar to thermally crosslinked/decomposed phenolic/furfuryl alcohol resins. The carbon structures were generated at 600°C. The low content of O is due to intermolecular rearrangements caused by C–C bond cleavage (Trompowsky et al., 2005). The P, Si and K contents are due to incorporation of lysophospholipids and minerals from original rice flour (Tester et al., 2004). These findings match well the FTIR spectrum data.

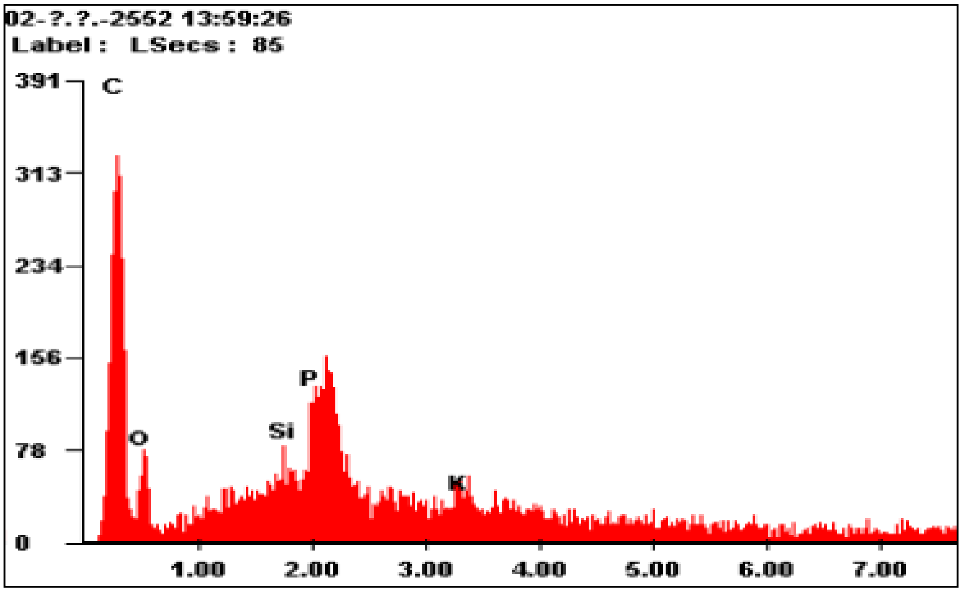

Figure 6. EDS spectrum of 90 µm rice flour charcoal carbonized at 600℃.

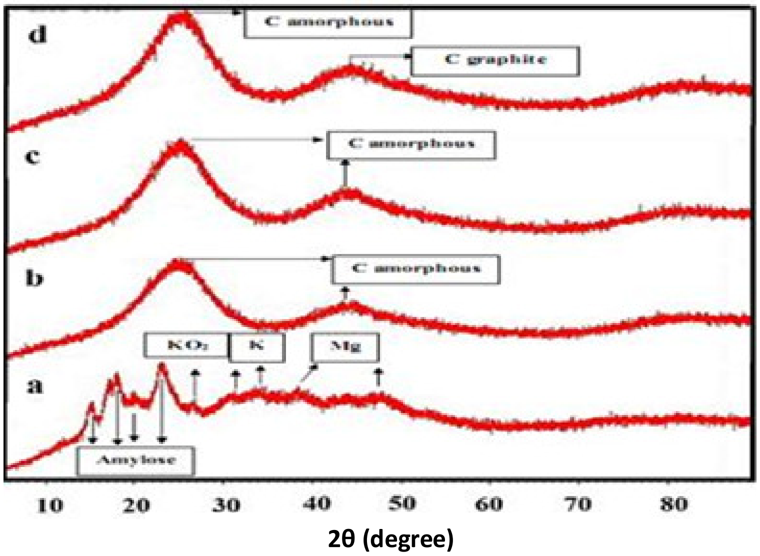

Figure 7. X-ray powder diffraction spectra of (a) fresh rice flour, (b) 90 µm rice flour charcoal with carbonization at 600℃, (c) 75 µm rice flour charcoal with carbonization at 600℃ and (d) 38 µm rice flour charcoal with carbonization at 600℃.

XRD analysis

Figure 7 shows the effects of starch powder size on the XRD patterns. The XRD patterns show ordered structures of the crystalline on the fresh rice flour. The diffractogram (Figure 7a) shows the content of amylase and amylopectin (cellulose) in fresh rice flour by peaks at 2θ = 15, 18, 20.3 and 23.5° (Zabar et al., 2009). These peaks almost disappear after carbonization (Figure 7b to d). This shows that the crystalline of fresh rice flour have been destructed and degraded to be amorphous carbon during the carbonization. It can be seen that two broad peaks centered around 26 and 44° occur, which correspond to the 002 and 10 reflections of disordered micrographite stacking (Zhang et al., 2008). Furthermore, this reveals the same graphite diffraction peak (a small sharp peak at 44°), which indicates that some amorphous carbons transform to graphite crystalline structures

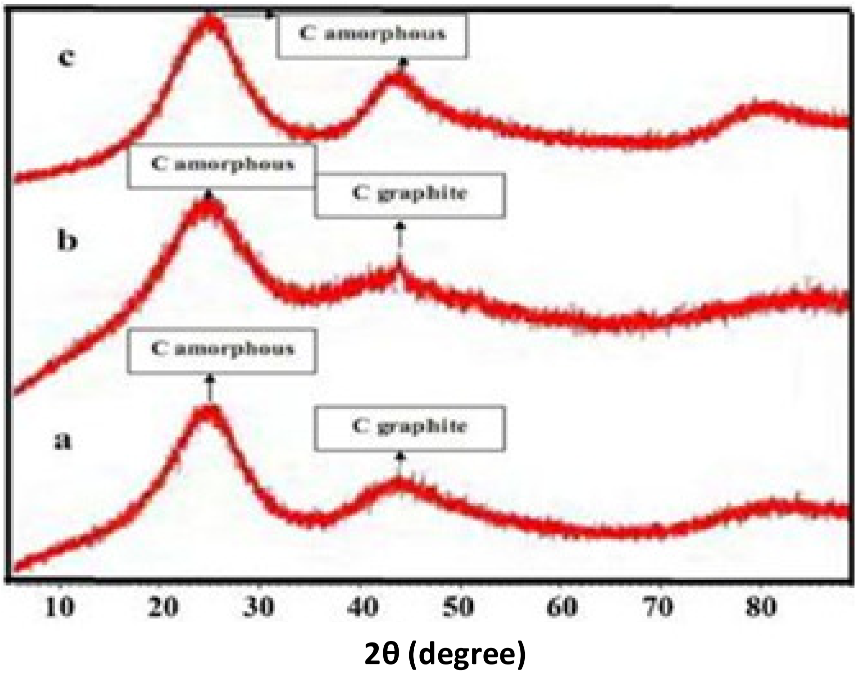

Figure 8. X-ray powder diffraction spectra of (a) 38 µm rice flour charcoal with carbonization at 600°C, (b) 38 µm rice flour charcoal with carbonization at 700°C and (c) 38 µm rice flour charcoal with carbonization at 800°C.

(Xingzhong et al., 2010). The very weak peak at about 32° is the pattern of the principal K_2CO_3 compound which occurs from KO_2 and K after carbonization (Díaz-Terán et al., 2003). The peak of Mg occurs at 38 and 47° of fresh rice flour.

The XRD patterns for all charcoals with different size (Figure 7) and carbonization temperatures (Figure 8) are very similar. This indicates that the 600 to 800°C carbonization temperatures and 38 to 90 µm starch powder sizes do not affect the structure of charcoals.

Conclusion

Starch charcoals with different sizes of powder were prepared by carbonization of starch at 600, 700 and 800°C. The results of this research show that the resulting carbonized products are amorphous carbon. The agglomerate nanocarbonfibrils and some carbon granules exist outside the surfaces of all charcoals. The nanocarbonfibrils are shaped like a snake and warp with diameters and lengths in the range of 75 to 120 nm and 1.5 to 3.5 µm, respectively. Other structures of charcoal particles are quasispherical and polygonal in shape with diameters in the range of 0.05 to 2 µm. There is a possibility that the natural nanocarbonfibriles are promising candidates in such applications as reinforced materials, adsorbents, supercapacitors and hydrogen storage.

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