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The Production and Characterization of Carbon Composite from Coconut Shell Charcoal

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Abstract

Structure and chemical composition of coconut shell carbon with polyvinyl alcohol (PVA) as the stimulant through the observation of TG-DTA, SEM-EDS, FTIR and XRD had been studied. The process was carried out by calcining coconut shell charcoal at the temperature of 873 and 1023 K under nitrogen flow, then mixed with polyvinyl alcohol (PVA) under composition of 2.5 to 7.5% wt. in water solvent. The development of carbon composite structure was observed by heating the samples in Argon gas of 1673 K, the rate of temperature was 10 K/min in 3 hours. The products were then analyzed by TG-DTA, SEM-EDS, FTIR and XRD. The result showed that the products were in uniform particle size of micrometer dimensions and spherical particles in shape, with average content of C element at 97.44% wt., aromatic character and semi-crystalline structure.

Keywords: coconut shell carbon, PVA, carbon composite, TG/DTA, SEM/ EDS, FTIR, XRD.

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Introduction

Carbon materials can be used in various applications, such as electrodes, catalyst supports, adsorbents and filters. Recent fact shows that it can be used as precursors for reaction which forms materials composite and structural ceramics (Lin and Yen, 2007). The advanced carbon materials such as synthetic carbon composites obtained from carbon fibers struggle to be accepted in wider practical use. Of well known carbon materials, the role of composite carbon cannot be overestimated either in modern industrial practice or in everyday life. It happens due to the unique physical and chemical characteristics of composite carbon which attract researchers to conduct certain research which explores those characteristics (Inagaki, 2000).

The structure of chemical bonds that is formed contributes to the establishment of superior properties of carbon materials (Buchman and Bryant, 1999). Carbon contains allotrope which has different types of chemical bonding structure, including graphite, diamond, black carbon, fullerene, carbon nano tubes (CNT). Graphite is a type of carbon material obtained from carbon atoms with sp^2 orbital. One of these atoms forms a new bond with 3 carbon atoms. The microscopic material consists of graphite flat sheets from carbon atoms which are bonded, as the graphene. The characteristics of the bond structure and dynamic interactions between the graphene layers produce strong electrical conductivity properties (Buchman and Bryant, 2002) which functions as a lubricant.

The heating process, using various methods, has conducted to accelerate the adsorption of electron (Hirose *et al.*, 2002). The mechanism can be as the simple as removal of surface impurities, however it may also involve the removal of oxide and even the structural rearrangement (Sahajwalla *et al.*, 2004). The use of temperature from 1000°C to 1720°C results in the increase in ratio of graphite layer in the crystallites from 4.5 to 33 and the growth in diameter from 1.8 to 6.3 nm.

Carbon used in the industry is an example of carbon that can be heated at temperatures up to 1000 - 1300°C, while graphite is a type of carbon which can be heated at temperatures higher than 2500°C. Heating at higher temperature of 3000°C will produce carbon that has an irregular structure which evolves to a more ordered graphite structure by removing the impurities of volatile material (Elsayed *et al.*, 2007).

Composite carbon can be obtained by carbonizing coconut shell, and polyvinyl alcohol (PVA) in a thermal decomposition process (Scok *et al.* 2005; Tae-Hwan *et al.*, 2002). The main composition of coconut shell consists of cellulose, lignite, and hemicelluloses with a formula C, O, H, and N. These organic materials contain functional groups such as hydroxyl (R-OH), alkanes (R-(CH_2) nR'), carboxyl (R-COOH), carbonyl (R-CO-R'), ester (R-CO-OR'), linear and cyclic clusters ether (ROR') with a variation of carbon (van der Marrel and Beutelspacher, 1976). In this process, the cellular anatomic features of coconut shell and polyvinyl alcohol are retained in the new carbon material (Inagaki, 2000). The structural changes during carbonization and the physical properties of the resulting chars have been investigated in several studies.

Polyvinyl alcohol (PVA) as an inert and organic adhesive is used to obtain high density products. PVA was chosen due to its homogeneity in functional groups, linearity and solubility in water (Ilcin *et al.*, 2010). With increasingly high-temperature treatment of adhesive polyvinyl alcohol (PVA), it further affects the growth of grain to be larger in size.

This study used coconut shell charcoal as raw material which functions as carbon to examine the growth of crystal in the development carbon composite. To obtain carbon from coconut shell charcoal, tar impurities and volatile material are removed. The removal of impurities is conducted by high temperature heating up to 600 - 1000°C. This heating is also aimed to eliminate the compounds carried by the drainage of gas. During the heating process, all non-carbon materials must be removed to form a pure carbon as well as to arrange the structure (Wiratmoko and Halloran,

2009; Ebner *et al.*, 2004). The removal of metals can be carried out by soaking the carbon in a solution of HCl (Fraga *et al.*, 2002).

Heating process of coconut shell will produce a gradual change. In the first stage of the carbonization, the carbon samples become coke. The second stage is graphitization, in which coke is changed into graphite carbon whose irregular structures tend to grow (over the graphite whose structure is irregular) (Gupta *et al.*, 2005; Miyazaki *et al.*, 2005). The nature of carbon depends on its source (Kang *et al.*, 2007), and on the method and conditions of synthesis (Lalena *et al.*, 2008). The nature of carbon materials gives impact on their various uses, primarily as carbon electrodes and carbon material structure.

This study discusses the use of, coconut shell and polyvinyl alcohol (PVA) to produce carbon composite materials (carbon bio-composite). The main purpose of this research is to study the crystal structure and chemical composition of carbon composite as affected by using parameters such as concentration of polyvinyl alcohol and sintering temperature.

Materials and Methods

A. Materials

This study used coconut shell charcoals as the raw material produced by PT. Tropica Nucifera Industry Bantul Yogyakarta, Indonesia. This charcoal is the source of carbon and polyvinyl alcohol. Further, Merck stimulant and argon gas were used as inert atmosphere to get air free.

Calcination was conducted using a tube-Thermolyne Furnaces (Sybron) Type 21100 with a maximum temperature of 1200°C. Calcinated charcoal as raw material was obtained through 100 mesh grinding and sifting. For carbon materials, Tarno compacted Grocki 312 model a maximum of 20 tons was used. Sintering was carried out by using a Carbolite furnace-Edwards Pirani 501 A6D 1600°C maximum temperature with argon gas as the atmosphere, Scanning Electron Microscopy (SEM) JOEL JSM-6360 LA and Energy Dispersive Spectroscopy (EDS) system JOEL JED-2300, and thermal reaction with TG/DTA METTLER. To study the spectrum of carbon materials, the Fourier Transform Infra Red (FTIR) Shimadzu model IR-Prestige 21 was used while the Goniometer model difractometer with Cu K_α (α = 1.54056 Å) radiation was used for X-ray Diffraction (XRD) analysis.

B. Methods

1. Preparation and Charcoal Calcination

Carbon powder 100 mesh sieves was calcined in an inert state through two stages. First, was the calcination at temperatures of 873 K for 3 hours with the existence of nitrogen gas then followed by the purification of charcoal powder which was extracted for 24 hours with 1 M hydrochloric acid at room temperature (Gupta *et al.*, 2005). The sample was washed with distilled water until it reached constant pH and was dried in an oven at temperatures of 383 K overnight (Fraga *et al.*, 2002). Re-calcination was carried out for 3 hours at temperature of 823 K with nitrogen.

2. The process of carbonization.

The carbon powder was calcined with 2.5 to 7.5% wt. polyvinyl alcohol then suspended in distilled water at 353 K and stirred for one hour. Binder system was mixed with charcoal powder, forming a paste with the density in different systems. The next step was molding by using a cylindrical mold with a diameter of ~ 15 mm. Compaction was performed with one direction force by the means of Tarno Grocki with the thrust of 5 tons. In this stage, the process produced a sample of pellets (green compact). The samples were then dried at room temperature for one day before oven drying for 4 hours at 383 K. The samples were then fed into a carbollite furnace for sintering at the temperature of 1273 K. The rate of temperature was 10 K/min and reaction time was 3 hours. Then, these samples were cooled in the furnace at a rate of 8 K/min, with a flow of argon gas. This process produced dense coconut shell coke or carbon-carbon composite materials (Wiratmoko and Halloran, 2009; Miyazaki *et al.*, 2005; Mothe and de Miranda, 2009).

3. Synthesis of carbon structures

The coke sample was heated for the 2nd time by sintering at 1473 K, 1673 K with a flow rate of 10 K/min, holding time of 3 hours, in the furnace Carbollite, with the furnace cooling rate of 8 K/min, under argon gas flow (Mendez and Santamaria, 2008).

Results and Discussion

Thermal Analysis

Figure 1 showed TG/DTA measurements for the coconut shell carbon, polyvinyl alcohol and carbon-PVA mixed with various compositions at temperatures ranging from 30 to 1500°C. Figure 1(a) showed DTA curve of the coconut shell carbon with endothermic reaction at peak temperatures of 48.20°C when the water is dissolved. The pure polyvinyl alcohol was obtained by the two endothermic peaks shown in Figure 1(b). The decomposition of material had occurred in polyvinyl alcohol under phase I of water molecules evaporation at the peak temperature of 255.76°C and phase II at a temperature of the release of H_2 and O_2, peak at 398.37°C (Thomas *et al.*, 2001). The first endothermic peak occurs in the temperature of 255.76°C, a transition commonly called temperature decomposition which was consistent with literature values of 230°C (Weast, 1970). The TG-DTA thermogram of carbon-polyvinyl alcohol (2.5 and 5% wt.), showed the decrease of endothermic peak.

The shape of the mass loss curve for the inert atmosphere was consistent with the generally accepted two-step mechanism for the degradation coconut shell carbon-PVA and polyvinyl alcohol. The first step in the mass loss curve results from the elimination of water (Mothe and Santamaria, 2009). In the second step, in the inert atmosphere, pyrolysis occurs to produce some organic volatiles which were resulted in the second mass loss step (Thomas et al. 2001; Saito and Takanori, 2004). The inert atmospheres of the material residues are respectively 93.8104, 10.5387 and 92.7250 % this expected to be since pyrolisation results in the formation of amorphous carbon or semicrystallin carbon (Rampe *et al.*, 2010).

SEM-EDS analysis

Figure 2 and 3 showed the SEM photographs of coconut shell surface carbonized at 1023 K and carbon composite (C/PVA) sintered at 1673 K, respectively. Figure 2 showed that coconut shell carbon was non-homogeneous particles distribution. Figure 3 showed a homogeneous and even surface morphology. The carbon composite from coconut shell carbon/polyvinyl alcohol (PVA) sintered at temperature of 1673 K exhibited uniform particle size of micrometer dimensions and spherical particles shape (Lin and Yen, 2007). It was also shown in Figure 3 that the morphological features of carbon particles appeared to be more irregular, characteristics as a typical of carbon particles (Inagaki, 2000).

EDS analysis for both the coconut shell carbon calcined at 1023 K and carbon composite, carbon/PVA (5% wt.) sintered at 1673 K were shown in Figure 4 and 5, respectively. It was apparent that chemistry composition of the coconut shell carbon (Figure 4) consisted of C element up to 95.29% wt. with average of C element was 94.97% wt. The carbon composite, carbon/PVA (5% wt.) (Figure 5) consisted of higher C element up to 97.72% wt. with average of C element was 97.44% wt.

Heat treatment ranging from 1023 to 1673 K, as demonstrated in this study, caused the aromatic layers grow and coalesce each other (Inagaki, 2000). This is due to the evolution of volatile matter (Rampe, *et al.*, 2011) and the breakage of cross-linking bonds such as CH_2 bridge.

FTIR Analysis

Figure 6 showed that the three spectra between charcoal (raw materials), charcoal results in HCl washing, and calcination charcoal (750°C, atmospheric nitrogen gas) that has been dried at a temperature of 120°C. All three spectra gave the peak absorption bands that basically have the same pattern. Peak absorption bands that always exist continuously on the wave number of 3425.58 cm^{-1} showed stretching vibration of OH groups on the surface of the

Figure 1. TG-DTA thermogram (a, f), PVA a pure (b, e), coconut shell carbon/PVA 7.5% wt (c, d) coconut shell carbon

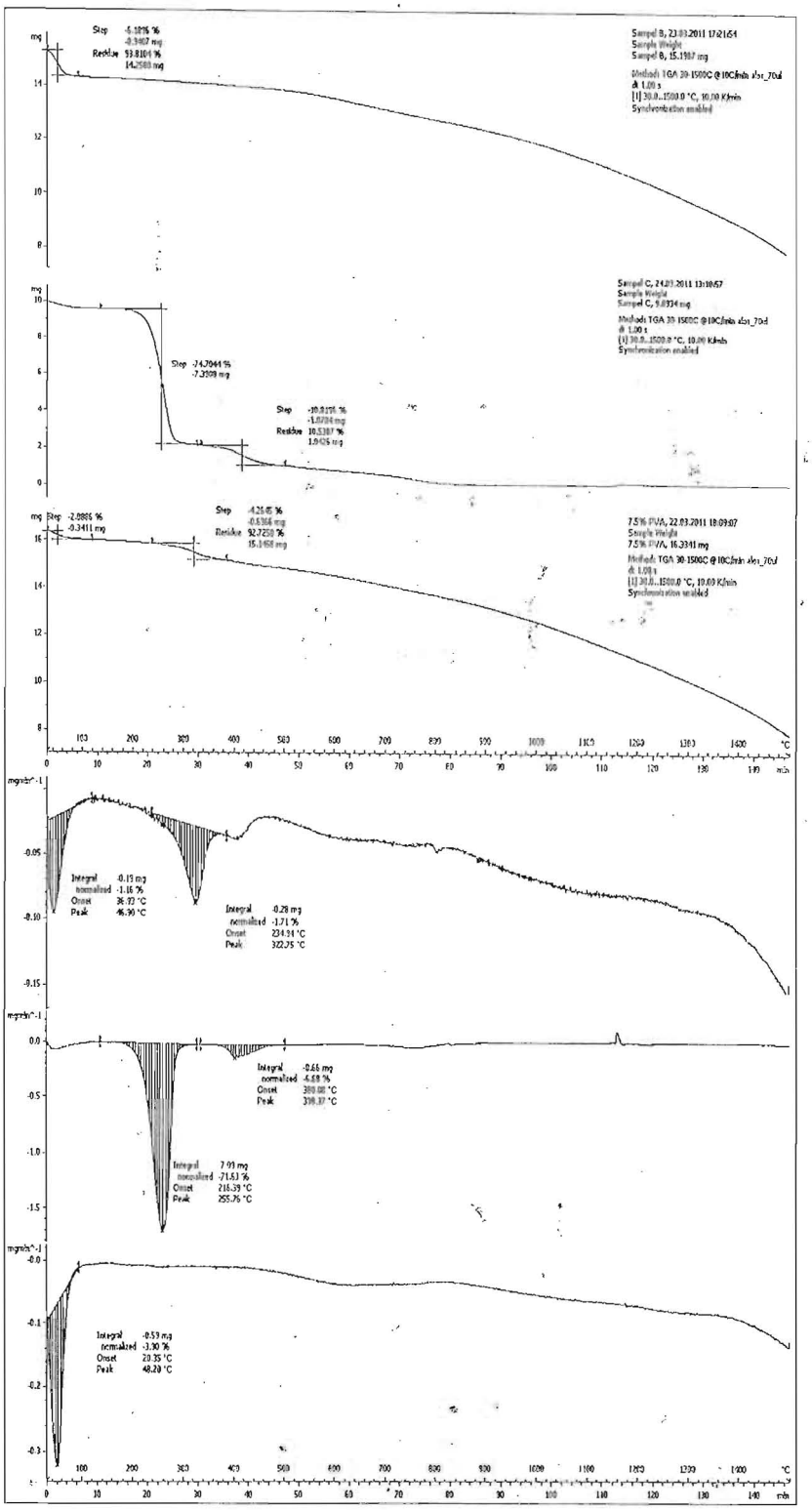


Figure 2. SEM micrographs of coconut shell carbon calcined at 1023 K

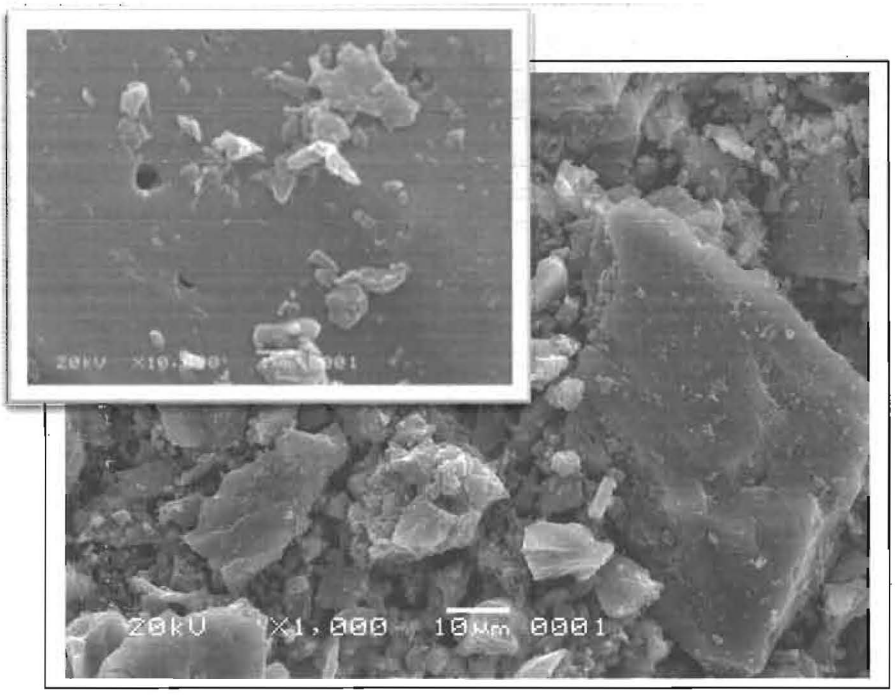


Figure 3. SEM micrographs of coconut shell Carbon/PVA (5% wt.) sintered at 1673 K

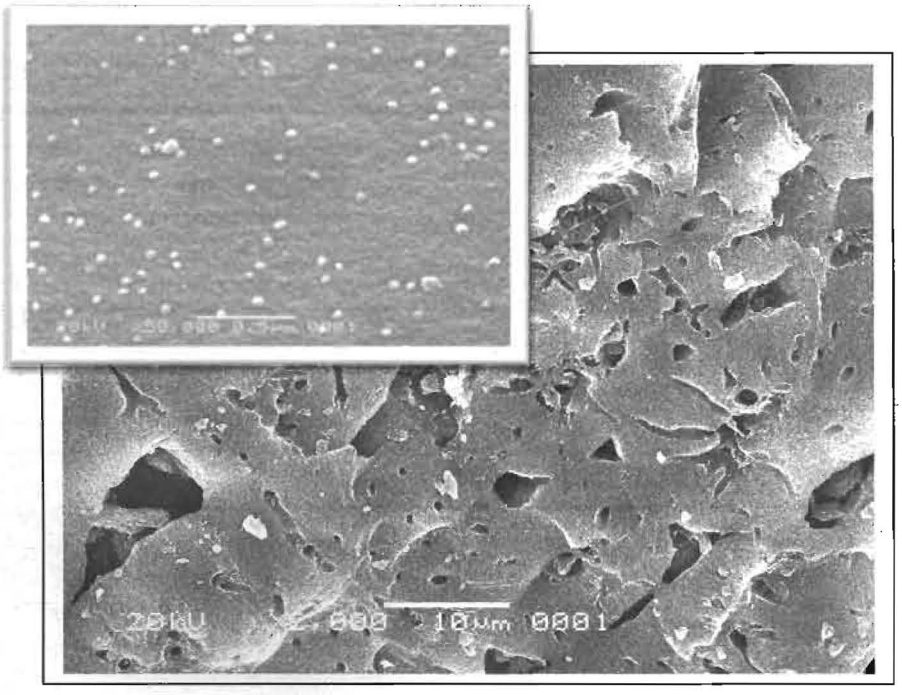


Figure 4. EDS analysis of the coconut shell carbon calcined at 1023 K, atmosphere Nitrogen

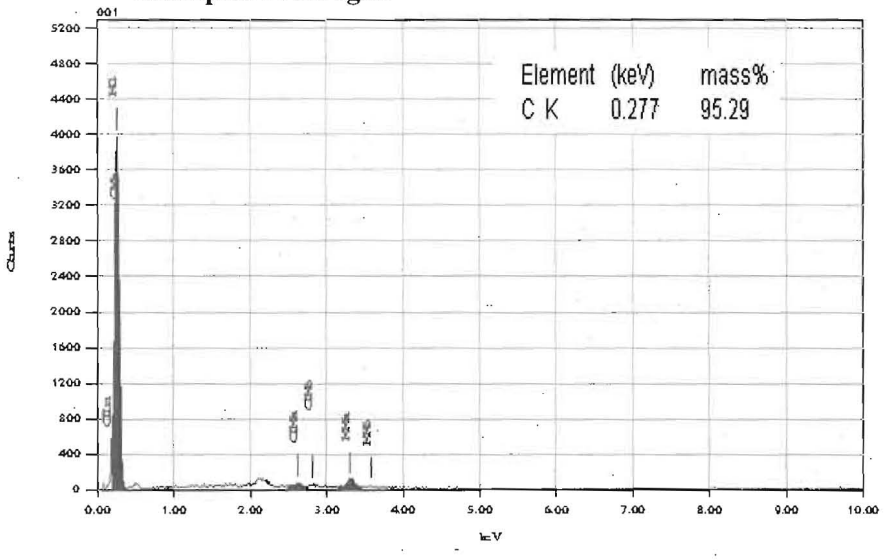


Figure 5. EDS analysis of the coconut shell carbon/PVA (5% wt.) sintered at 1673 K, atmosphere Argon

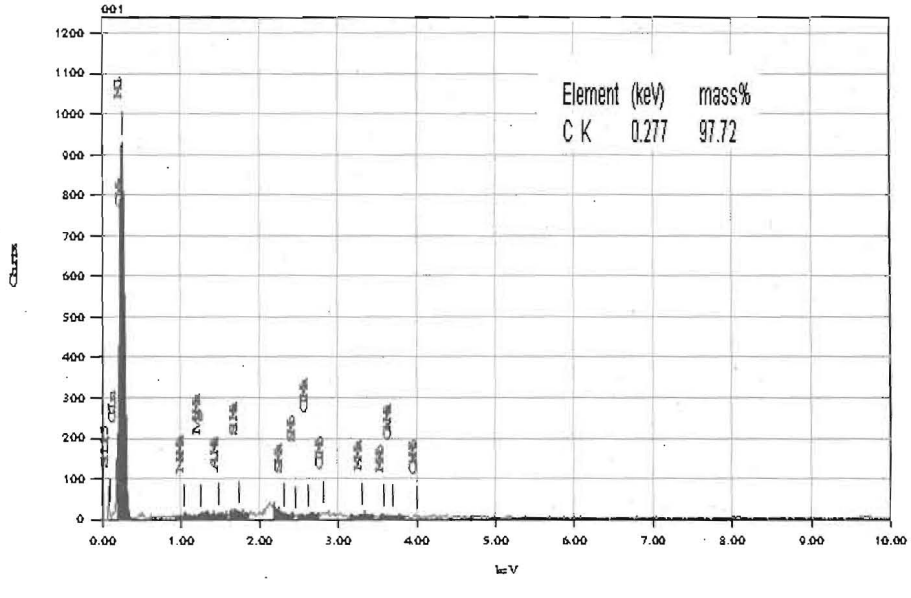


Figure 6. FTIR spectra pattern of carbon and PVA, solvent method, sintering 1673 K, Argon atmosphere: (a) raw material of charcoal, (b) charcoal calcined at 1023 K, (c) raw material carbon, (d) 2.5% wt. PVA, (e) 5% wt. PVA, and (f) 7.5% wt. PVA

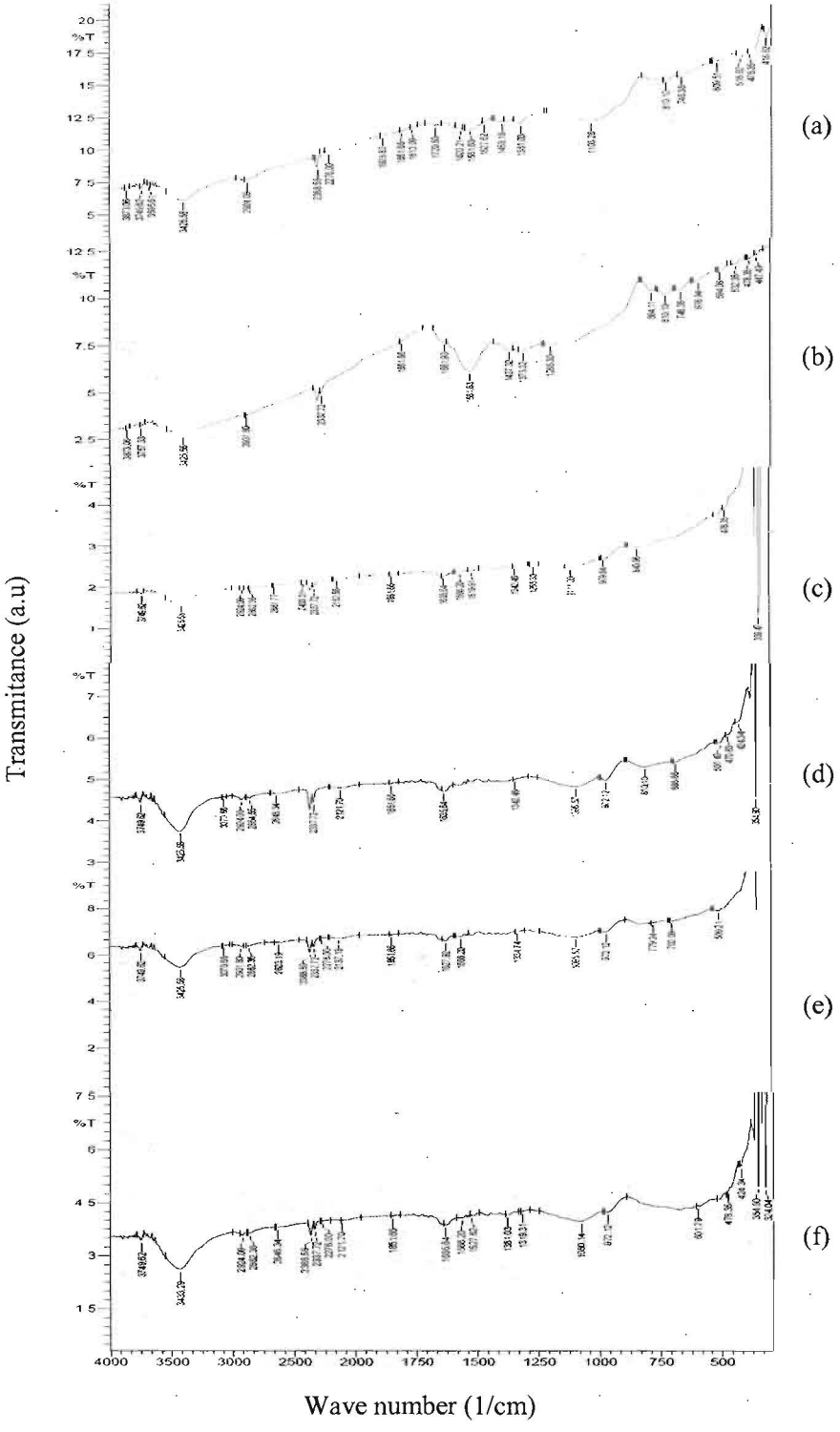
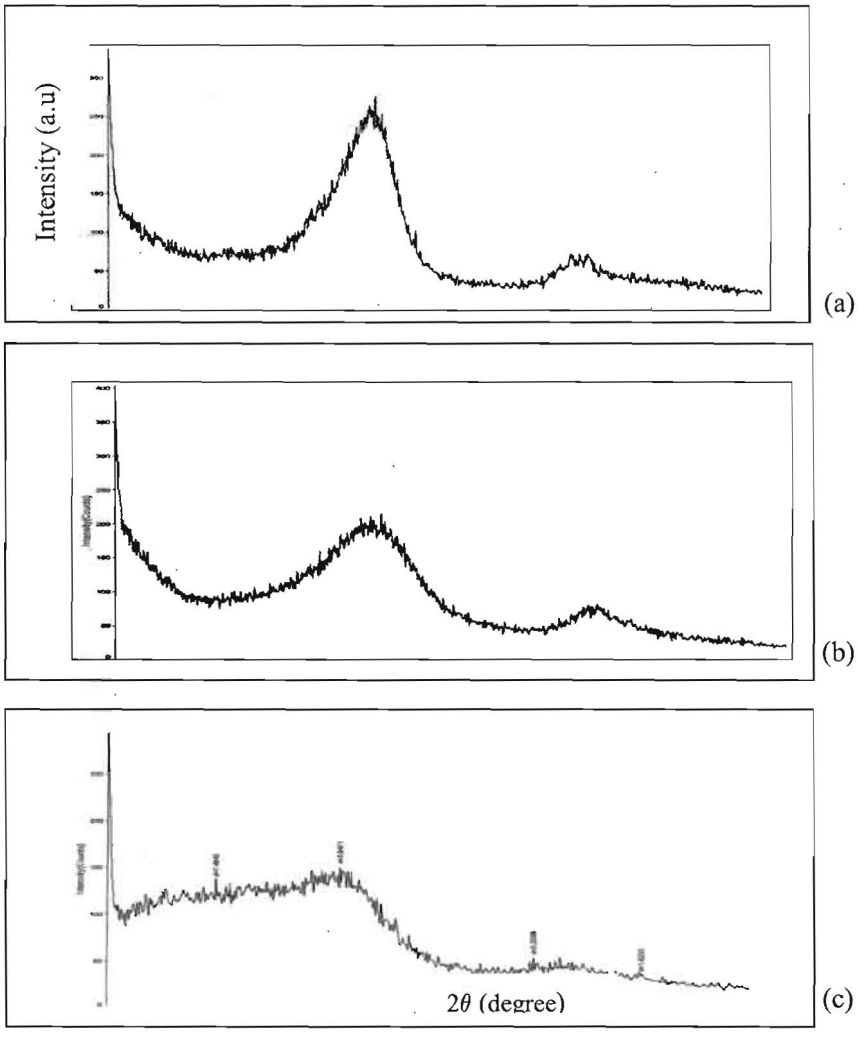


Figure 7. XRD pattern of: (a) coconut shell charcoal, (b) carbon calcined at 750°C (N_2), and (c) carbon sintered at 1000°C (Ar)



outer and inner bound to the elements of C contained in charcoal (such as carbon black) or can be water that is absorbed on charcoal [24, 25]. Ribbon uptake 2931.50 cm^{-1}; 2337.72 cm^{-1} was a weak band, 1581.63 and 1103.28 cm^{-1} sharp and very strong characterizes the C-C stretching vibration found in the structure of carbon black.

FTIR spectra pattern of carbon composite produced by solvent method with PVA stimulant concentration of 2.5, 5 and 7.5% wt. sintered at (1673 K, reaction time 3 hours, argon atmosphere, annealing) was shown in Figure 6 (a-d). The spectra showed a broad band near 3425 cm^{-1} which indicated the presence of hydroxyl groups on the carbon surface. The stretching was attributed to the absorbed water on the surface of coke and carbon black. The stretching frequencies of the aromatic C=C and aromatic C-H groups gave rise to peaks at 2924 and 2862, respectively, which were originally existed as the support for the coke and graphite (van der Marrel and Beutelspacher, 1976; Rampe, *et al.,* 2011). The peak at near 1600 cm^{-1} ($\upsilon_{C=O}$) along with another peak at 1635 cm^{-1} (υ_{C-O}) indicated the presence of carboxylic acid groups. The peak at 1635 cm^{-1} was assigned to a conjugated hydrogen bonded carboxyl groups,

assigned by several authors on coke. The peak at 2924 cm^{-1} was due to C-H stretching of CH_2 groups (Maria and Teixeira, 2009). The bands near 1600 cm^{-1} indicated the fingerprint region of C=O, C-O and C-H groups that exist as functional groups of coke and carbon black. The band near 972 cm^{-1} was due to out-of-plane bending of C-H group in benzene derivatives (Mothe and de Miranda, 2009).

XRD analysis

Figure 7 showed a typical X-ray diffraction (XRD) pattern of testing charcoal, calcined carbon and coke carbon material that sintered at temperatures 1000°C. XRD diffractograms of charcoal, calcined carbon and coke carbon material gave value of interlayer spacing (d) (Å) as a graphite semi-crystalline structure. Yin *et al.* (2009) reported that the decrease of the (d) and the increases of the crystalline diameter and average stacking height of the aromatic carbon sheets (L_c) with increasing the temperature suggested the development of stacking structure, increased the size of crystallite as well as removal of defects and increased order in carbon materials structure. The increase of L_c with increasing temperature resulted from crystallite growth in-plane and coalescence of crystallites. In this process, the structure of amorphous carbon structure was changed into semi-crystalline structure with a better degree of order, namely turbostatic structure (Rampe *et al.*, 2010). There was the change of internal structure by setting the position of equilibrium carbon atoms.

Conclusion

Carbon composite can be prepared from carbonized coconut shell and polyvinyl alcohol (PVA). The result showed that the products were in uniform particle size of micrometer dimensions and spherical particles in shape, with average content of C element at 97.44% wt. on 5% wt. PVA concentration (chemical composition), aromatic character and semi-crystalline structure. Increasing sintering temperature, the structure of amorphous carbon structure was changed into turbostatic structure with a higher purity level.

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