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Preparation and Characterization of White Carbon Black From Rice Husk

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Abstract

Generally white carbon black in a form of silica is used instead of carbon black as reinforcing filler for rubber compounding. In the present research white carbon black was prepared from rice husks in cost effective method with direct incineration of acid leaching rice husk. The physico-chemical properties of rice husk and the product of white carbon black obtained from rice husk were investigated by Thermogravimetry, Particle size analyzer, Scanning electron microscope; Fourier transformed infrared radiation (FTIR), X-ray fluorescence and X-ray difractometry analyses. It was found that the decomposition of organic constituents of rice husk was revealed by Thermo gravimetric and carbon, hydrogen, nitrogen, sulpher (CHNS) analyses. The FTIR spectrum showed presence of Si-O-Si band with a strong peak at 1085 cm^{-1}. The analysis of particle size and scanning electron microscope demonstrated that the produced white carbon black represent different size of 112 µm to 0.01 µm with very small nano-particle and amorphous structure. The amorphous structure of product was also confirmed by XRD pattern. The high pure product as 99.9% was confirmed by XRF analysis. These types of product have potential application as filler in rubber compounding.

Key words: Amorphous silica, Rice husk, Silica and White carbon black

Introduction

Rice Husk (RH) is the outer layer of rice grain, which is the waste product of the rice milling process (Rohani *et al*., 2015). Various utilization of RH have been reported, but mostly it is used an alternative fuel for energy production, production of activated carbon and as a raw material for manufacture of industrial chemicals based on silica and silica compounds (Chungsangunsit *et al*., 2010; Kumar *et al*., 2012; Ghosh and Bhattacherjee, 2013). Silica and silica powder obtained from RH have much potential application in many industrially important products. White carbon black (WCB) is one of the applicable products of RH. WCB is a form of silica ($SiO_2.nH_2O$) that is used instead of carbon black mainly in rubber compounding. The product is very finely divided and reactive. It is mainly use as a catalyst, catalyst carrier, decolorizer, delustering agent, reinforcing agent for rubber, filling agent for plastics, thickening agent for printing ink, softness polishing agent for metal, filler for insulation and heat insulation, and filler for advanced cosmetics and spraying materials (Kejing *et al*., 2013). It is an industrial gourmet powder for improving the quality of products in rubber. However the utilization of WCB depends on the quality and particle size of the product. For example the product size about 30 to 50 µm can be used only in production of general rubber while the ultrafine products size less than 10 µm can be used as a reinforcing agent in high-grade rubber products, because of their large specific surface area, strong linking ability, good dispersity, and good optic and mechanical properties.

In rubber compounding, fillers are major additives, because it enhances the tensile strength, modulus, tear strength, abrasion resistance, and stiffness of such properties of the product. Different material have been used as a filler to reinforce natural and synthetic rubber such as carbon black, clay, shale, synthetic and precipited amorphous white silica, recycled rubber powder, graphite (Ismail *et al*., 2002; Kim *et al*., 2003; Ansarifar *et al*., 2006; Yang *et al*., 2006; Pan *et al*., 2015). Agricultural by-products has also been used as a filler, this included banana peel, rice husk, spent mango, bean seed skin and groundnut shell (Adeosum, 2002); cocoa pod and rubber seed shell, ash of rice husk (Ismail *et al*., 2001) etc. In the vulcanization of rubber, usually carbon black used much more than that of others. The origin of carbon black from petroleum which causes pollution and gives rubber black and expensive (Isaac and Augustina, 2011), while the processing of agricultural by-product likes RH is flexible, economical and ecological.

In global context, annual rice husk production is about 137 million tones whereas Bangladesh produces about 9.0 million tons (FAOSTAT, 2011). Around 22% of the paddy mass is husk and the major constituent of rice husk are hydrated silicon and organic materials consisting of 55-60 wt % of cellulose and hemicelluloses and 22 wt % of lignin. During the process about 20% mass of rice husk remains as ash and this contains 80-95% amorphous silica. Therefore, in the present study RH has been considered as a source of silica and this attempt has been made up for WCB production from RH. Several methods for preparing WCB from RH have been reported. But most of them are uneconomical and need huge energy. Moreover various research studies concerning the silica production and application of RH have already been made, but there are still contradictory regarding the optimum condition of production and its relationship with the properties of the final RH (Rosario *et al*., 2012). In this consensus, production of high reactive pure silica, some conditions are crucial in order to obtain an amorphous structure and the absence of unreactive carbon. This paper reports a comprehensive characterization of WCB produce from RH in cost effective method simply by burning under appropriate condition to achieve a good quality product.

Materials and Methods

Materials

The raw material RH was collected in a nearby rice mill. All reagents used were analytical grade and purchased from local agent of Merck Germany Co. Ltd. Sample was prepared by proper washing and thermal treatment procedure and characterized by standard method.

Preparation of WCB

The collected RH was washed thoroughly with clean tap water to remove the soluble particles, dust, and other contaminants present, whereby the heavy impurities such as sand was also removed. It was then dried in an air oven at about 60^{o}C for 24 h. The dried RH was grinded to made sieve size at -45 µm. 100 g of fine grinding RH was mixed with 800 ml of 10% HCl and refluxed them for 3 h by stirring frequently. It was cooled and standby for about 20 h. separated the residue by refrigerated centrifugation. Washed them with hot water and repeated the centrifugation until the residue became free from HCl. The residue was made moisture free by oven drying at 100^{o}C. The treated husk was burnt in an electric furnace by controlling the temperature so that it reached 700^{o}C in 1 h at heating rate 5^{o}C/min and continuing heating in additional 3 h at 700^{o}C. The desired product was obtained as a white powder.

Analysis of RH and WCB Silica

The silica and metallic impurities in the samples were analyzed by X-RF (model: Rigaku ZSX Primus, Japan). Particle size of the RH as well as product silica was measured by using a laser based particle size analyzer (model microtrac-S3500). Carbon, hydrogen, nitrogen and sulpher (CHNS) were measured by HEKAtech elemental analysis (model Euro EA-3000, Germany). The $O_{difference}$ was calculated air dry and ash free basis. Fourier transforms infrared spectroscopy FTIR spectra were recorder with KBr pellets using a WQF-510 FTIR Rayleigh (Beijing Rayleigh Analytical Instruments CO. Ltd., Beijing, China). The pH was measured with a Jenway pH meter (model Jenway-3510, UK). Chemical phases were identified by X-ray diffractometer (XRD) (model Bruker-D8 Advance) using a Cu-K□ radiation source (□=1.5406Å).

Results and Discussion

Characterization of RH

RH mainly comprises with organic constituents as celluloses, hemicelluloses and lignin and the remaining residue contains silica with small amount of metallic oxides. Iyenagbe *et al*., 2012 reported the average composition of RH which is given in Table 1. The amount of constituents of RH varies rice to rice as well as it depends on the rice variety, soil chemistry, climate condition and the geographic localization of the culture (Iyenagbe and Othman, 2012). On the other hand, a typical analysis results of experimental RH are shown in Table 2 which gives tremendous idea about silica and organic constituents as carbon, hydrogen, nitrogen, sulpher and oxygen difference of RH. Table 2 showed as-received moisture content of experimental RH was 8.5% and ash 19.32%, which content desired product SiO_2. The elemental analysis of RH showed C, H, N, S was 33.48%, 4.66%, 0.59%, and 0.04%, respectively which indicated the high organic constituent's presents in RH.

Table 1. Composition of RH

Constituent	Wt (%)
Celluse	35
Hemicellulose	25
Lignin	20
Crude protein (N×6.25)	3
Ash	17

The chemical composition of RH as-received and the RH treated with 10% HCl and finally heated at 700^{o}C at a rate of 10^{o} C min^{-1} for 4h was analyzed by X-RF. The resulting data has showed in Table-3, which demonstrated 90% SiO_2 present in as-received RH, 93% present in HCl leaching RH, while 99.9% SiO_2 was obtained by heating of HCl treated RH. A traces of elements were found in an order RH (As- received)> RH (HCl leaching)> RH (Heating of HCl treated RH), which indicated that the heats with HCl treated RH gives high pure and high concentration of SiO_2 than that of direct heating of as-received RH.

Table 2. Properties analysis of RH

Parameters	RH
Moisture%	8.5
Ash%	19.32
C%	33.48
H%	4.66
N%	0.59
S%	0.04
$O_{diff.}$ %	33.41

Table 3. Chemical composition of RH with different condition

Composition (wt %)	RH (As received)		RH (HCl leaching)		RH (After burning)
	Direct X-RF analysis data	Calculated data on LOI	Direct X-RF analysis data	Calculated data on LOI	
SiO_2	84.35	11.60	93.73	16.57	99.90
Al_2O_3	2.33	0.32	0.22	0.038	0.04
Cr_2O_3	0.82	0.11	0.14	0.024	0.01
CaO	2.83	0.39	1.20	0.212	0.02
SO_3	0.26	0.045	0.17	0.030	-
Fe_2O_3	2.63	0.36	0.70	0.123	0.02
K_2O	2.36	0.32	0.20	0.035	0.01
ZnO	0.04	0.005	0.08	0.014	-
MgO	1.71	0.23	-		-
MnO	0.27	0.037	-		-
Rb_2O	0.03	0.004	-		-
NiO	0.07	0.012	-		-
CuO	0.01	0.0017	-		-
TiO_2	0.14	0.024	-		-
Na_2O	0.21	0.037	-		-
P_2O_5	1.94	0.344			
LOI	-	86.24	-	82.32	ND

Thermogravimetric (TG) analysis of RH

TG analysis was used to determine the existence of organic components in the RH. The TG curves of RH are shown in Fig. 1. This showed initial weight loss occurs within the range of 0-100^o C with a weight loss of about 2-5% correspondence to loss of water and other volatile substances. The second stage revels a rapid and large weight loss at temperature between 150 -350^{o}C and gives 40-50% weight loss. This is due to the thermal decomposition of hemicelluloses and cellulose as a major organic component in the RH. Because hemicelluloses decompose mainly at 150 – 350^o C while cellulose at 275 – 350^o C reported elsewhere (Shafizadeh *et al*., 1976; Antal, 1983). The third stage showed a weight loss of about 25% that could be due to lignin, a thermally more stable aromatic polymer which undergoes gradual decomposition between 350-750^{o}C. The residual of ash is mainly the non-combustible silica.

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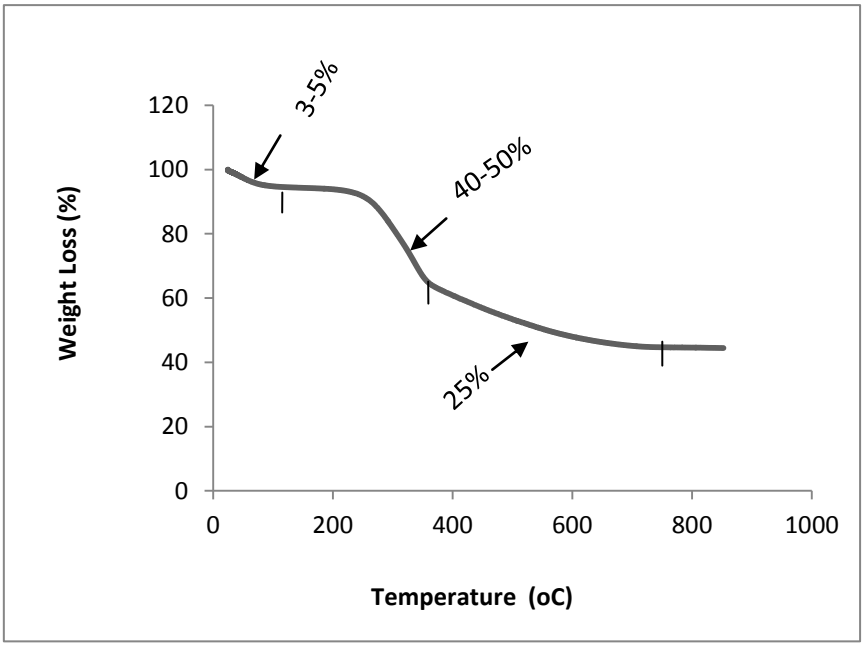


Fig. 1. Thermo gravimetric (TG) curves of RH

FT-IR analysis of RH and WCB

FTIR spectrum of WCB are shown in Fig. 2. In this figure the peaks at 1,116 cm^{-1} and 845 cm^{-1} are due to Si-O-Si asymmetric and symmetric stretching modes, respectively. Typical bands of product WCB shows O-Si-O stretching at 1085 cm^{-1}, 1167 cm^{-1} and 845 cm^{-1} and bending vibrations at 610 cm^{-1}. A broad band's at 3450-3600 cm^{-1} and a band at 1733 cm^{-1} corresponded to the O-H stretching and bending vibrations. The band centered at 610 cm^{-1} is due to the bending frequency of Si-O-Si. A large broad band around 3600 cm^{-1} was attributed to the presence of the O-H stretching frequency for the silanol group and the remaining adsorbed water. A band around 1733 cm^{-1} was assigned to the bending vibration of water molecules bound to the silica matrix. The FTIR spectra show C-H peaks at 2880 cm^{-1} and 2955 cm^{-1}, clearly indicating the organic modification of the nanoparticle surface and the silica nanoparticle obtained in amorphous state.

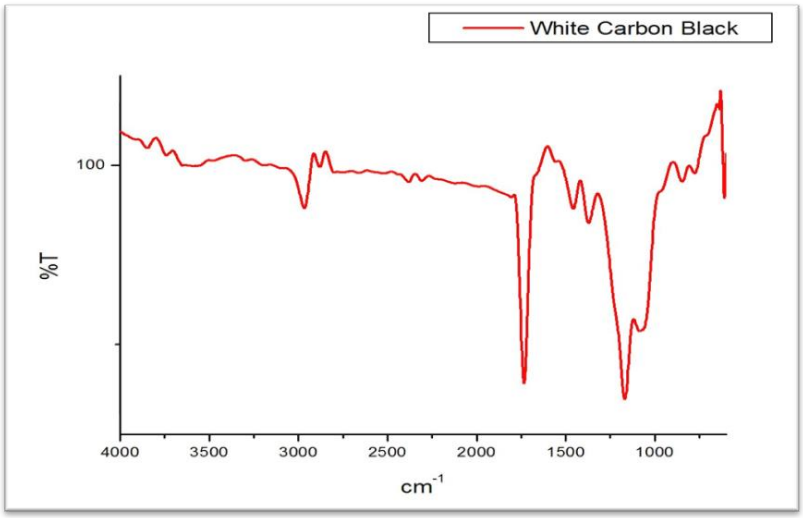


Fig. 2. FTIR pattern of WCB

Particle size analysis of WCB

The particles of the product WCB are not equal in size. As shown in Fig. 3 the maximum size of particle was observed 112 µm, while minimum was 0.01 µm and showed high concentration than that of maximum size. The specific surface area was shown 115.8 m^2kg^-. These findings indicate that the particles of silica were agglomerates of small nano range particles and forming globules platelets of varied sizes.

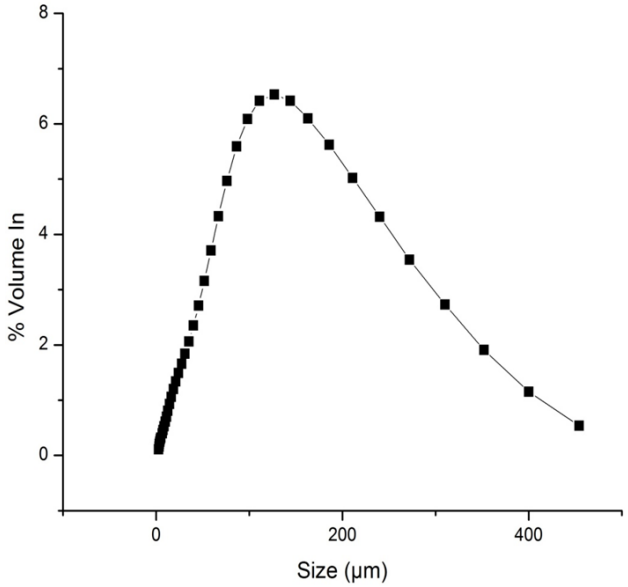
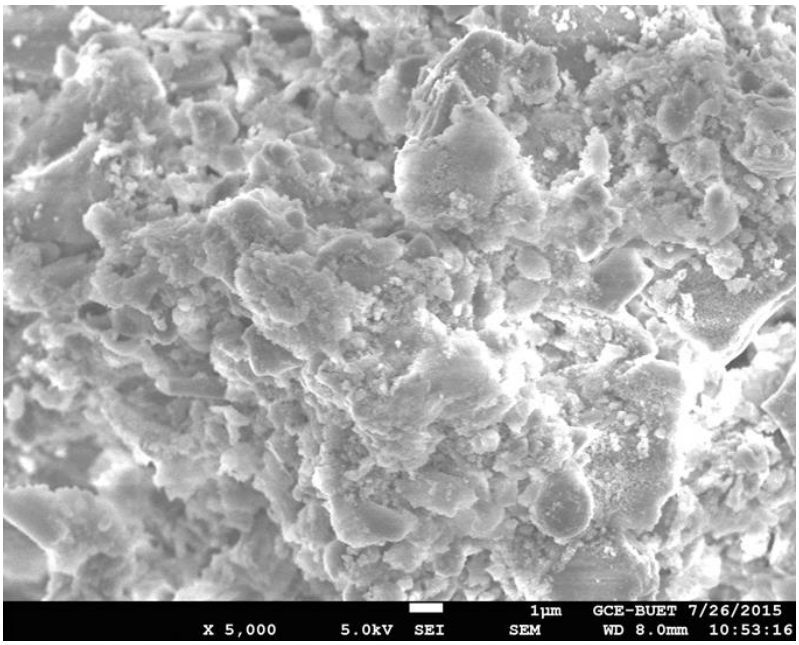


Fig. 3. Particle size distribution of WCB

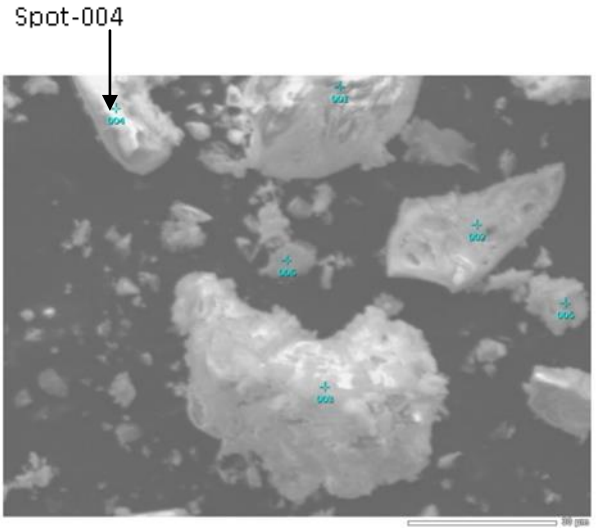
SEM-EDAX analysis

The morphological structure as well as atomic wt% of prepared WCB was analyzed by SEM-EDAX which is shown in Fig. 4. Generally silica which is formed by incinerating rice husk above 800^o C is crystal (Kalapathy *et al*., 2002; Olamide and Oyawale, 2012). In the present research silica was obtained as WCB by heating at 700^o C. So the morphological features of the

amorphous silica were observed in Fig. 4.a. as cluster form and/or fine globules and/or platelets with multifaceted particle shape and size. It seems that particle of silica are agglomerates of small nano-range particle. Atomic wt% of the elements of silica cluster was measured from the spot-004 as shown in Fig. 4.b and summarized in Fig. 4.c. Which showed atomic wt% of Si and O were 53.35% and 46.55%, respectively, indicating the WCB as silica obtained from rice husk was 99.9% pure.



a. FESEM Micrograph of WCB



b. EDAX of WCB Spot- 004

Element	Atomic%
O	46.55
Al	-
Si	53.35
K	0.02
Ca	-
Cr	-
Fe	-
Zn	0.08
	100

c. EDAX analysis of WCB

Fig. 4. SEM-EDAX photograph: **a)** FESEM Micrograph of WCB. **b)** EDAX of WCB Spot- 004. **c)** EDAX analysis of WCB

XRD analysis

The phase identification of desired product WCB was assessed by XRD in Fig. 5. The pattern showed a broad peak at $2\theta = 22^{o}$ and no defined sharp peaks due to crystalline were encountered, confirming the results from the silica activity index allowed to conclude that the silica produced from RH has an amorphous structure.

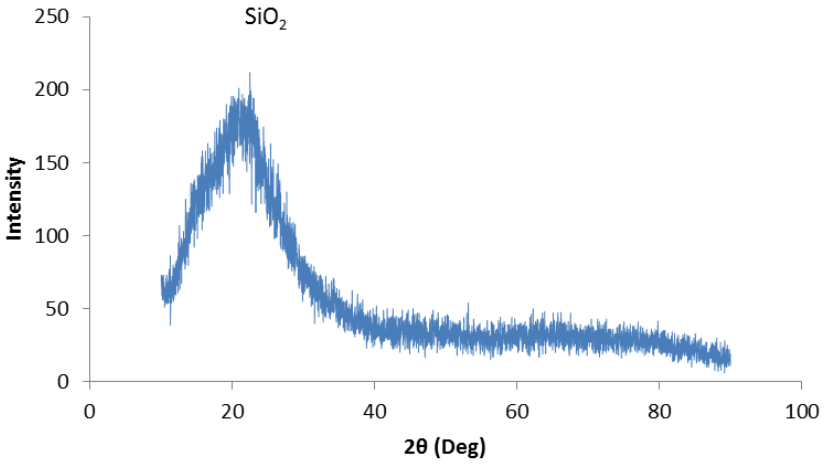


Fig. 5. XRD pattern of WCB

Conclusions

In the present study, WCB was prepared by direct incineration of acid leaching RH with optimum heating condition at 700^{o} C for 4h at 5^{o} Cmin^{-1} heating rate. The product was conducted with different experiments for characterization. The experimental results showed that the prepared WCB was amorphous in structure with nano and/or micro level particle in size and 99.9% pure with large surface area. These might be useful as filler for plastic and rubber compounding.

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