

# Thermal and Elemental Evaluation of Modified Coconut Shell Fibre in Natural Rubber Reinforcement

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**Abstract** - The influence of carbonization on the modification of coconut shell fibre has been investigated using thermogravimetry, x-ray fluorescence, chemical sorption and mechanical analyses. Carbonization was effected at various temperatures of 300, 400, 500, 600 and 700°C for three hours each. The characteristics of the resulting fibre were evaluated and compounding natural rubber composites achieved. The result showed that increase in carbonization temperature to a maximum of 600°C leads to the burning off of lignocelluloses through thermal degradation and then eventually stabilising the particulate filler. The contributive increase of Potassium oxide (K<sub>2</sub>O) with a final improvement on the reinforcing potential of coconut fibre was evaluated. Chemical properties and mechanical properties of hardness, abrasion resistance, tensile strength, modulus and flexural indices also increased with carbonization temperature. Composites reinforcement in engineering applications using modified coconut shell fibres especially in aerospace, transportation, construction and automobile devices is highly recommended.

**Keywords:** Carbonization, Composites, Modification, Reinforcement, Rubber.

## 1.0 INTRODUCTION

Agricultural by-products mostly of cellulosic origin have been recognized as a potential renewable energy and a most likely filler for the development of engineering properties in natural rubber composites [1, 2]. Coconut fibre is a major palm waste found littered around in most part of Edo state, Nigeria. Appropriate modification has been shown to have influence on performance of biodegradable fibres used in natural composites [3].

Despite the inherent green strength available in natural rubber, raw dry rubber is rarely used in its original state for any meaningful engineering and other functional applications [4]. One major additive usually built into rubber matrix for properties modification are a wide range of filler materials with various colours, reinforcements and diverse origin. The fillers themselves are positioned to perform better if appropriately modified [5]. Research is being carried out to replace most synthetic fibres with lignocelluloses fibres as reinforcing fillers [6-9]. Compared

to talc, silica, glass, carbon, and other synthetic fibres, the lignocelluloses fibres such as coconut fibres are light weight, easily available in expensive biodegradable and non-toxic [1, 10-11].

Various other works on the use of coconut fibre have also been reported; such as reinforcement materials in epoxy matrix [12]; effect of the fibre on cure characteristics, physico-mechanical and swelling properties of natural rubber vulcanisates [13]; mechanical properties of epoxy/coconut shell filler particle composites [14]; study of absorption of coconut shell powder-epoxy composites [15-17].

Coconut shell fibre is one such widely available agro-waste by product, which contains relative percentage of cellulose, hemicelluloses, lignin and Ash [18]. One of the major drawbacks with the use of agro-fibres like coconut shell fibre as a filling material is its hydrophilic nature, responsible for moisture absorption and consequent deformation of the product [19, 20]. This study sort to modify coconut fibre through carbonization at various temperatures in order to combat these inherent challenges. The thermal characteristics and resulting elemental oxides were monitored. Thus the aim of this present study is to prepare natural rubber composite material from carbonized coconut shell fibre with improved mechanical, thermal and chemical properties suitable for engineering applications. Thermogravimetry analysis, elemental oxides analysis using x-ray fluorescence, sorption test and mechanical analysis were conducted.

## 2.0 METHODS

### 2.1 Materials

The coconut shell fibre wastes used in this study were obtained from Auchi Edo State, Nigeria. All additives used for compounding were of the commercial grades. The crumb natural rubber which conforms to technically specified rubber (TSR10) was obtained from Rubber Research Institute of Nigeria, Iyanomo, Benin City.

## 2.2 Filler Preparation and Characterization

The coconut shell fibre was obtained, washed to remove sands and debris; and then dried at 95°C for 24 hours to remove moisture. A portion of the dried fibre was apportioned into 200g each for carbonization at 300, 400, 500, 600 and 700°C for 3 hours each for effective carbonization using the Gallenamp Cat no FR614 carbonization machine. A grinding mill was used to ground the portion of dried raw fibre and the other five (5) portions of the carbonized fibre. Particle size of 100µm was achieved using a 100µm rated aperture sieve. Some basic properties of the raw and carbonized fibres were obtained using ASTM standard methods for characterization. Table 1 indicates the characteristics of the coconut fibre.

## 2.3 Compounding and Rheological Examination

Homogenization, additives incorporation, dispersive and distributive mixing were achieved on the laboratory two roll mill (180 x 360mm) at a monitored temperature of 70°C with a speed ratio of 1:1.25. Sequence of addition and time of mixing of additives were kept uniform for the entire mixing cycle. Homogenization and mixing were carried out in accordance with ASTM-D3182 standard method. The compounded rubber sheets were then allowed for a 24 hours period of maturation at a temperature of 32°C prior to rheological examination to determine cure characteristics. The cure characteristics were measured at 165°C using an Oscillating Disc Rheometer (Alpha ODR 2000 Model) in accordance with ASTM-D2084 standard method. Press curing was eventually effected at a temperature of 150°C; pressure of 150kg/cm<sup>2</sup> and an average time of 15 minutes in order to obtain optimum cure. Press curing was done in accordance to ASTM-D1632-07.

## 2.4 Mechanical Properties

The mechanical measurements evaluated on the cured sheets using standard methods were: Shore "A" hardness (ASTM-D2240); Abrasion resistance (ASTM-D5963-04); Compressive strength (ASTM-D575-91); Tensile strength, Modulus, Elongation at break and Flexural analyses (ASTM-D3039/D). Measurements of mechanical properties were done along the grain direction and results indicated in Table 2.

## 2.5 Chemical Sorption Analysis

In order to determine the chemical resistance to the crosslinked network formed, a sorption/swelling test was conducted in accordance with ASTM-D3010 standard method. Vulcanized compositions were obtained as small sheets of about 1.5g and approximately (2x2x0.3) cm. The exact weights of dried samples both for the raw and carbonized types were measured prior to and after immersion in the selected solvents for 72 hours at 32°C. The

equilibrium swellings of the compound in percentages were mathematically gotten from the relation  $(W_2 - W_1 / W_1) \times 100$ ; where  $W_1$  and  $W_2$  are the initial weight and weight of the swollen sample respectively. See sorption values in Table 3.

## 2.6 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA50-Shimadzu) was carried out under N<sub>2</sub> atmosphere with a purge gas flow of 65cm<sup>3</sup>min<sup>-1</sup> from 32 to 800°C. Approximately 30g of each sample was used. The heating rate of the analysis was 10°C min<sup>-1</sup>. Fig. 1 shows the results of thermogravimetric analysis performed and table 4 shows TGA, biomass residue and percent lost at 800°C.

## 2.7 X-ray Fluorescence Analysis

The thermoscientific advant'x 1200 model was used. A 30mm flat disc of the sample was prepared. In order to reduce the effect of surface irregularities, the sample was spun 10rpm, and the Bragg's Diffraction condition was obtained. The binder used around the sample was Lithium tetra-borate (Borax). The pressing force was set at 240 Newton and the movement stroke was set at 6rpm. 45V and 40A were used and samples were run for 4 hours. See Table 5 for percentage elemental oxide composition and figure 2 for graphical representation.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Characterizations

As indicated in Table 1, P<sup>H</sup> of slurry at 32°C became more alkaline as carbonization temperature increased. The possible reason for this was that metal content activity increased leading to alkalinity as the residual materials were being lost on combustion [21]. Moisture content decreased with carbonization temperature because the high temperature of 300°C and above will cause the evaporation of any retained moisture and most of the -OH absorption band faces off [3]. Loss on ignition increased as the lignocelluloses got burnt off. Ash content also increased directly with carbonization temperature; which suggested why the carbonization was not taken beyond 700°C because ashing must have seriously commenced at about that temperature. Conductivity increased with carbonization temperatures as particles became more oriented and properly packed. Surface area increased with carbonization temperature as particle sizes became smaller and densely packed. Particle diameter, length, and width also became smaller with increase in carbonization temperature thereby providing a greater reinforcing ability [5].

Table 1: Characteristics of the Raw and Carbonized Coconut Fibre.

Parameters	CFP	300	400	500	600	700
PH of slurry @ 32 <sup>0</sup> C	6.32	6.32	6.55	7.10	7.25	8.02
Moisture content (%)	11.00	6.90	6.45	5.00	3.50	1.00
Ash content (%)	2.40	3.15	3.80	4.55	6.85	8.95
Loss on ignition 800 <sup>0</sup> C (%)	32.00	36.40	38.90	42.50	42.50	52.20
Conductivity (µm)	0.83	2.14	2.48	2.85	3.20	3.35
Length (µm)	0.38	0.30	0.28	0.22	0.15	0.09
Width (µm)	0.02	0.09	0.06	0.04	0.03	0.01
Diameter (µm)	0.05	0.02	0.02	0.01	0.06	0.05
Lumen (µm)	0.01	-	-	-	-	-
Surface area (cm <sup>2</sup> )	0.07	0.19	0.34	2.15	2.90	3.16

### 3.2 Mechanical Properties

The mechanical properties are shown in Table 2. Hardness values increased with carbonization temperature as particle sizes decreased. The finer aggregates created interaction between the filler particles and the polymer matrix [6]. Tensile strength, modulus abrasion resistance, and flexural strength increased with increase of carbonization temperature and decrease of filler aggregation. This was possibly due to the fact that the coconut fibre particles strengthened the interface of the rubber matrix as the carbonization temperature increased. The mechanical properties of the composites were a function of several

combinations of factors such as the stress- strain behaviours of the fibre and matrix phases, the phase volume fractions, the fibre concentration, the distribution and orientation of the fibre relative to one another as carbonization temperature increased [22, 23]. The chain stiffness accounted for lower elongation at break with increased in carbonization temperature because of closer adherence of the filler to the polymer phase. The chain stiffening leads to high resistance to the strength when strain is applied [21, 23].

Table 2: Mechanical Properties of the Composites

Properties	CFP	300	400	500	600	700
Hardness (Shore A)	64.00	68.00	75.00	79.00	80.00	76.00
Abrasion resistance index	20.40	25.32	29.95	32.40	36.55	34.15
Compression set (%)	26.92	24.65	20.96	19.85	19.46	22.85
Tensile strength (MPa)	5.96	7.25	7.97	8.45	8.68	7.85
EAB (%)	520.50	515.80	498.20	488.50	455.70	468.85
Modulus (MPa)	2.85	3.20	3.84	4.22	4.25	4.00
Flexural strength (MPa)	1.99	1.65	1.42	1.40	1.38	1.48

### 3.3 Chemical Sorption Analysis

Results for the sorption test of the composites are presented in Table 3. The fundamental differences in the composites sorption values with increased carbonization temperature could be related to size, proportions and orientation of the particles in the rubber matrix [23]. Composites showed

more resistance to swelling in benzene and least resistance in hexane because of the solubility parameters of the solvents in relation to the composites. The further apart their solubility parameters the more resistance to swelling as it became difficult for the solvent to penetrate the crosslinked network of the composite matrix [7].

Table 3: Sorption Test Results

Carbonization Temperature (°C)	Hexane (%)	Xylene (%)	Toluene (%)	Benzene (%)
CFP (32 °C)	525	520	495	312
300	500	492	445	258
400	485	490	415	218
500	425	472	358	201
600	412	422	325	198
700	415	425	368	200

### 3.4 Thermogravimetric Analysis

Figs. 1(a) and (b) as well as Table 4 show the result of the thermogravimetric analysis performed on the raw and carbonized coconut shell powder. Fig. 1 (a) gives the percentage of weight loss as a function of carbonization temperature, while Table 4 presents the derivative values for thermal degradation, residue and percent weight loss at 800°C. Water loss was observed around 100°C, and further thermal degradation takes place as two-step process. In the first step, the degradation of hemicelluloses present in the coconut shell powder takes place at around (300-400)°C. At about (400-500)°C, the main degradation of cellulose occurred and a prominent peak appears beyond a slight shoulder in Fig. 1(b) at the temperature corresponding to the commencement of maximum decomposition rate around 75 % weight loss of lignocelluloses. According to Kim et al, 2006, the depolymerisation of chain stiffened hemicelluloses occurs between 180 and 350°C, the random

cleavage of the glycosidic linkage of cellulose between 275 and 350°C and degradation of lignin between 250 and 500°C.

The burning-off of the lignocelluloses which has random amorphous structure [2] gradually gave way to an improved crystalline region which improves the thermal stability of the coconut shell powder. The lignin component of the lignocelluloses, which represents the last component to decompose at 500°C has a high thermal stability and difficult to decompose [24].

From Table 4; as the carbonization temperature increases, a considerable fraction of the lignocelluloses gets burnt-off; the residue diminishes and the percentage losses of lignocelluloses increase. Increase percentage loss improved the crystalline region and consequently the reinforcements in the mechanical properties of the composites [10].

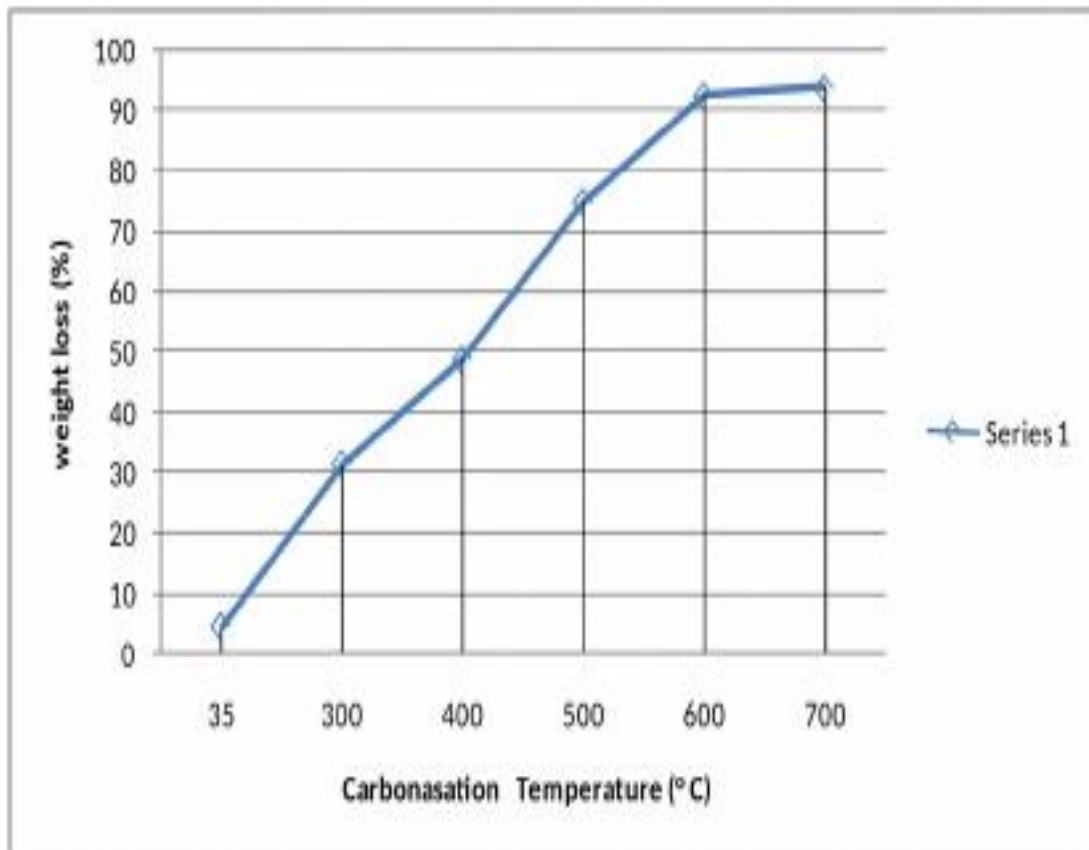


Figure 1 (a): TGA Curve showing percentage of weight loss (Lignocelluloses)

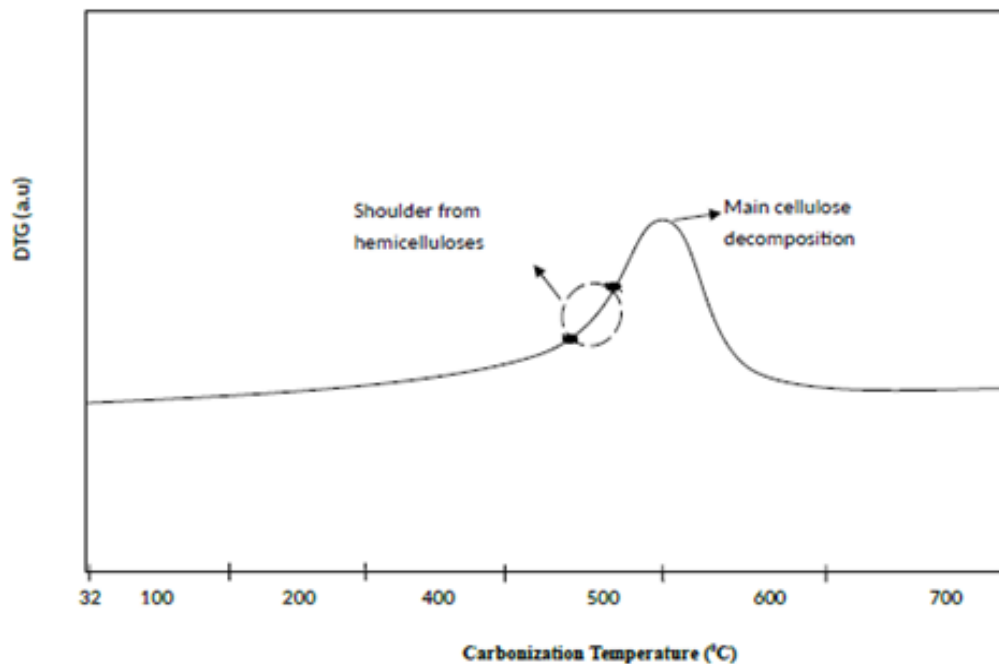


Figure 1 (b): DTG Curves of shoulder and peak of coconut shell fibre as a function of carbonization temperature.

Table 4: Thermal Degradation Values, Residue and Percent Loss at 800°C for the Raw and Carbonized Coconut Shell Fibre

CFP	Sample Weight (mg)	Loss Value (mg)	Residue (mg)	Percentage Loss (%)
Raw (32°C)	30	1.8	28.2	6
300°C	30	9.4	21	31.3
400°C	30	14.6	15	48.7
500°C	30	22.5	9	75
600°C	30	27.8	3	92.7
700°C	30	28.2	2.7	94

### 3.5 X-Ray Fluorescence Analysis

Table 5 and Fig 2 shows the results of the major elemental oxide of SiO<sub>2</sub>, K<sub>2</sub>O and FeO<sub>3</sub> present in the coconut shell fibre. All other oxides indicated at the bottom of the Table also existed but in traceable and minute fraction. X-ray fluorescence spectroscopy opens the possibility to get additional information of the carbonized coconut shell fibre in an attempt to investigate the fibre network [24].

The raw coconut shell fibre has a higher percentage of Fe<sub>2</sub>O<sub>3</sub>, followed by K<sub>2</sub>O and then SiO<sub>2</sub>. Carbonization temperature decreased Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>; but increases K<sub>2</sub>O. The raw coconut shell fibres consist of 80% elemental oxide of Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and K<sub>2</sub>O; while the carbonized coconut shell fibre consists of 70% Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and K<sub>2</sub>O put together. Increased in carbonization temperature diminished Iron and Silicon oxides but increases Potassium oxide.

The concentration of Potassium oxide which is highly electrovalent on the carbon surface (from carbonization) is changed by contact of Oxygen at a higher temperature resulting in a marked enhancement in catalytic activities and therefore contributing to the reinforcement of the composites [25]. The ionization energy of Potassium oxide increases with increase in carbonization temperature and leading to greater and stronger interpenetrating network between the carbonized coconut shell fibre and the composite matrix. This kind of interpenetrating network enhances the mechanical, thermal and chemical properties of natural rubber composite [20, 26-27].

Table 5: Percentage of Major Elemental Oxides Composition in Raw and Carbonized Coconut Shell Fibre

Elemental Oxides	CFP	300	400	500	600	700
SiO <sub>2</sub>	20.00	17.03	16.75	15.99	11.52	12.04
K <sub>2</sub> O	27.30	42.44	41.32	45.44	58.65	62.03
Fe <sub>2</sub> O <sub>3</sub>	33.11	13.87	13.59	12.94	2.30	3.20

\*All other available Oxides such as TiO<sub>2</sub>, CaO, SO<sub>3</sub>, NiO, P<sub>2</sub>O<sub>5</sub>, MnO, Al<sub>2</sub>O<sub>3</sub>, Cl, CuO, Re<sub>2</sub>O<sub>7</sub>, ZnO, Yb<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, BaO and MoO<sub>3</sub> exists at trace and negligible values.

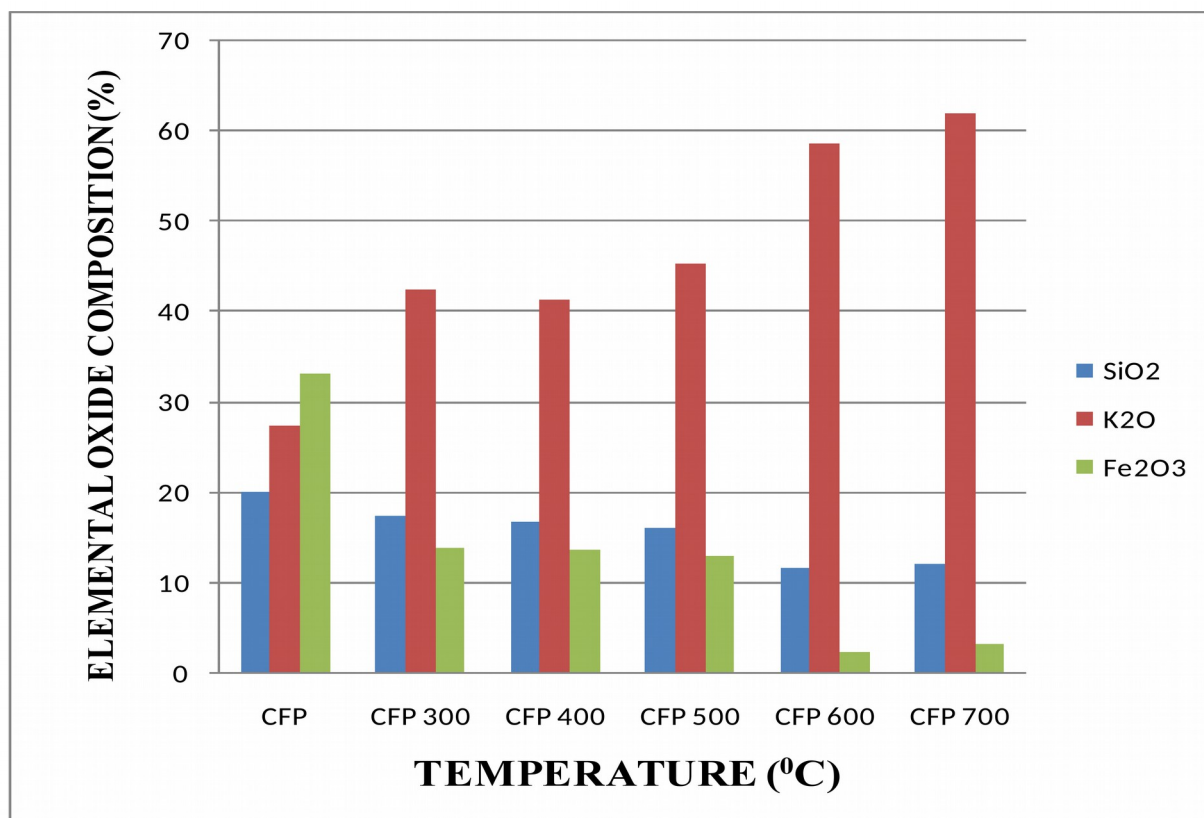


Figure 2: Graphical Representation of Percentage Elemental Oxides as a Function of Carbonization Temperature

#### 4.0 CONCLUSION

According to the thermogravimetric and X-ray fluorescence results of the analyses of the raw and carbonized coconut shell fibre, we can say that carbonization brought about modification by burning off lignocelluloses and removal of elemental oxides which hinders filler-matrix interpenetrating network interactions. Improvement was made on factors contributing to composite reinforcement interactions; hence the noticeable enhancement of mechanical properties such as hardness, abrasion resistance, tensile strength, modulus and flexural strength as well as improvement in sorption properties as carbonization temperature increase to a maximum of 600°C. The depolymerisation of cellulosic macromolecules and electrovalent energy interaction of Potassium oxide

occurred due to the impact of carbonization on the coconut shell fibre.

#### REFERENCES

- [1] H. G. B. Premlal, H. Ismail and A. Bahariu. A Comparison of the Mechanical Properties of Rice Husk Powder Filled Polypropylene Composites with Talc Filled Polypropylene Composites. *Poly. Test.* 2002, 21 (7), 833-839.
- [2] Y. Han-Seung, K. Hyun-Joong, P. Hee-Jun, L. Bum-Jae, H. Taek-Sung. Water Absorption Behaviour and Mechanical Properties of Lignocellulosic Filler- Polyolefin Bio-Composites. *Elsevier, Composite Structures.* 2006, 72, 429 - 437.
- [3] A.K. Mohanty, M. A. Khan, and G. Hinrichsen. Surface Modification of Jute and its Influence in Performance of Biodegradable Jute-Fabric/Biopol Composites. *Sci. Technol.* 2002, 60(7) 1115-1124.

- [4] M. Ahmedna, M. Johnson, S. J. Clarke, W. E. Marshel, and R. M. Rao, R.M. Potential of Agricultural by-Product Based Activated Carbon for Use in Raw Sugar Decolonization. *J Sci Food Agric.* 1997, 75, 117-124.
- [5] S. Husseinsyah and M. Mostapha. The Effect of Filler Content on Properties of Coconut Shell Filled Polyester Composites. *Malaysian Polymer Journal.* 2011, Vol.6 No 1, 87-97.
- [6] M. M. Thwe and K. Liao. Effects of Environmental Aging on the Mechanical Properties of Bamboo-Glass Fibre Reinforced Polymer Matrix Hybrid Composites. *Comp.* 2002, A33, 43-52.
- [7] B. D. Park, S. G. Wi, K. H. Lee. Characterization of Anatomical Features and Silica Distribution in Rice Husk Using Microscope and Micro- Analytical Techniques. *Biomass and Bioenergy* 2003, 25, 319-327.
- [8] A.K. Rana, A. Mandal, and S. Bandyopadhyay. Short Jute Fibre Reinforced Polypropylene Composites: Effects of Compatibiliser, Impact Modifier and Fibre Loading. *Comp. Sci Tech.* 2003, 63, 801-806.
- [9] 9. A.C. N. Singleton, C. A. Baillie, P. W. R. Beaumont, and T. Pejis. On the Mechanical Properties, Deformation and Fracture of a Natural Fibre/Recycled Polymer Composite. *Comp.* 2003, B34, 519-526.
- [10] E.T.H. Vink, K.R. Rabago, D. A. Glassner, and P.R. Gruber. Application of Life Cycle Assessment to Nature Works Polylactide (PLA) Production. *Poly. Degra. Satiability.* 2003, 80, 403-419.
- [11] R. Md. Rezaur, I. Md. Nazrul, H. Md. Monimul, H. Sinin, and S. A. Abu. Effect of Chemical Treatment on Rice Husk Reinforced Polyethylene (PE) Composites. *Bio resources.* 2010, 5(2), 854-869.
- [12] O. A. Jacob, H. Ayogu, M. S. Olawale. Evaluation of Mechanical Properties of Coconut Shell Fibre as Reinforcement Material in Epoxy Matrix. *International Journal of Engineering Research & Technology.* 2014, vol. 3, Issue 2, 2337-2348.
- [13] P. A. Egwaikhide, E. E. Akporhonor, and F. E. Okieimen. Effect of Coconut Fibre Filler on the Cure Characteristics, Physico – Mechanical and Swelling Properties of Natural Rubber Vulcanisates. *International Journal of Physical Sciences.* 2007, vol.2 (2), 039-046.
- [14] S. M. Sapuan, and M. Harimi. Mechanical Properties of Epoxy/Coconut Shell Filler Particle Composites. *The Arabian Journal for Science and Engineering.* 2003, vol. 28, No. 2B, 171-181.
- [15] S. Alok, S. Savita, K. Aditya. Study of Mechanical Properties and Absorption Behaviour of Coconut Shell Powder – Epoxy Composites. *International Journal of Materials Science and Applications.* 2013, Vol.2, No. 5, 157-161.
- [16] K. S. Pradhan, S. E. Dwarkadasa, J.P. Reucroft. Processing and Characterization of Coconut Shell Powder Filled UHMWPE. *Materials Science and Engineering; A Journal.* 2004, 367(1-2) 57-62
- [17] J. O. Agunsoye, S. I. Talabi, O. M. Sanni. Study of Mechanical Behaviour of Coconut Shell Reinforced Polymer Matrix Composites. *Journal of Minerals and Materials Characterization and Engineering.* 2012, 774-779.
- [18] P. V. Joseph, G. Matthew, K. Joseph, G. Groeninckx, and S. A. Thomas. Dynamic Mechanical Properties of Short Sisal Fibre Reinforced Polypropylene Composites. *Comp.* 2003, A34, 275 – 290.
- [19] N. Chand, T. K. Dan, S. Verna, and P. K. Rohatgi. Rice Husk Filled Polyester Resin Composites. *J. Materials Science Letters.* 1987, 6(6), 733 – 735.
- [20] H. Ismail, M. Edyhan, and B. Wirjosentono. Bamboo Fibre Filled Natural Rubber Composites: The Effects of Filler Loading and Bonding Agent. *Poly. Test.* 2002, 21(2), 139-144.
- [21] M.D. Ayo, I. C. Madufor, L. O. Ekebafé, and M. N. Chukwu. Effect of Filler Carbonization Temperature on the Mechanical Properties of Natural Rubber Composites. *Researcher.* 2011, Vol. 3(11) 7-10.
- [22] J. Bhaskar and V. K. Singh. Physical and Mechanical Properties of Coconut Shell Particles Reinforced-Epoxy Composites. *J. Mater. Environ. Sci.* 2013, (2) 227-232
- [23] F. P. Momoh, P.A. P. Mamza, C. E. Gimba, C.E and P. Nkeonye. Morphological Trends of Modified Coconut Fibre in Natural Rubber Reinforcement. *Journal of Emerging Trends in Engineering and Applied Sciences.* 2016, 7(4):167-172.
- [24] A.C. Larson and R. B. Von Dreele. General Structure Analysis System (GSAS). *Los Alamos National Laboratory Report LAUR.* 1994, 86-748.
- [25] Y. Shin-ya, T. Ken-ichi and S. Minoru. Accumulation of Potassium Oxide on Carbon and Enhancement of Catalytic Activity for Isomerisation by O<sub>2</sub>. *J. Chem. Soc; Chem. Commun.* 1981, 1061-1062.
- [26] H. S. Iang, H. J. Kim, H. J. Park, B. J. Lee, and T. S. Hwang. Water Absorption Behaviour and Mechanical Properties of Lignocellulosic Filler-Polyolefin. *Biocomposites. Comp. Stru.* 2006, 72, 429-437.
- [27] H. S. Kim, S. Kim, H. J. Kim, H. S. Yang. Thermal Properties of Bio-Flour-Filled Polyolefin Composites with Different Compatibilizing Agent Type and Content. *Thermochim. Acta.* 2006, 451, 181-188.