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Morphology And Crystallinity Of Modified Coconut Shell Powder In Natural Rubber Development

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Abstract: ***In this evaluation study, Coconut Shell Powder was modified through Carbonization at varying temperatures of 300, 400,500, 600 and 700^{0}C for three hours each and used as fillers for property development in natural rubber compound. The carbonized and raw fillers were ground and passed through 100µm sieve to achieve the rated particle size. X-Ray Diffractometer (Shimadzu 6000 Model) and Scanning Electron Microscopy (SEM) were used to evaluate and monitor changes in amorphousness and crystallinity of the Carbonized fillers in order confirm modification trends in the mechanical and chemical properties of the composites. The X-Ray Diffraction patterns and SEM images clearly showed that structural modifications were effected in the Carbonized powder. Optimum performance were observed at carbonization temperature of 500^{0}C. Results achieved are significant at developing the mechanical properties of natural rubber compounds for use in engineering wares such as automobile shocks and suspenders, bridge bearings, industrial hoses, O-rings and heavy duty seals.***

Keywords: crystalline intensity, morphology, carbonization, composites and fillers.

I. INTRODUCTION

Natural rubber development has over the years present a major cause for concern in elastomeric development especially in the areas of engineering and technological applications. Natural rubber of course possesses some basic and fundamentally sort for properties which make it attractive to researchers and product developers/designers. The green strength of rubber is of an appreciable value, but yet modern trends in researches and product development consistently seeks a much more valuable use especially in the highly technical areas of applications. A major modifier needed in natural rubber development is the filler class. Fillers of different colours, reinforcement and origin had played a major role in natural rubber modification over the years. A direct development and structural modification of fillers usually leads to indirect modifications in natural rubber composites, and hence a development in engineering wares of natural rubber origin.

Researchers have published in available literatures various works on the application of natural fillers in composites such as pineapple, sisal, jute, cotton, bamboo, coconut shells, groundnut shells and wood flours fillers as the reinforcement in composites.

Jacob et al, 2014 reported the evaluation of mechanical properties of coconut shell fibres as reinforcement material in Epoxy matrix and established the possibility of using it as a new material for engineering applications. In 2011, Husseniyah and Mostapha reported the effect of filler content on properties of coconut shell filled polyester composites.

Their results showed that the tensile strength, Young's modulus and water absorption of polyester/CS composites increased with the increasing CS content but elongation at break decreased.

Onyeagoro, 2012 studied cure characteristics and physical-mechanical properties of carbonized bamboo fibre filled natural rubber vulcanisates. Results obtained showed that compatibilized carbonized bamboo fibre filled vulcanisates exhibited improvement in the cure properties investigated over the non- compatibilized vulcanization.

Egwaikhide et al, 2007 reported the effect of coconut fibre filler on the cure characteristics, physico- mechanical and swelling properties of natural rubber vulcanisation and the result showed that coconut fibre is potential reinforcing filler for natural rubber compounds.

In 2003, Sapuan et al reported the mechanical properties of epoxy/coconut shell filler particle composites and found out that the tensile and flexural strength of the epoxy coconut filler composites were affected by the amount of filler in the composites. The more the filler content, the higher the strength.

Bhaskar and Singh, 2013 carried out a study on physical and mechanical properties of coconut shell particle reinforced epoxy composite and reported that the mechanical properties-tensile strength and modulus of elasticity were closely related to physical property-density.

Alok et al, 2013 also study the mechanical properties and absorption behaviour of coconut shell powder-epoxy composites and concluded that the composite prepared with 20% to 30% CSP filled volume fraction was suitable for the application in interior part of an aircraft, motor car and auto mobile where materials with good tensile strength, low density and low hydrophilic characteristics are required.

Shuaibu and Mamza, 2016 worked on the characterization of polypropylene filled composite using scanning electron microscopy and x- ray diffraction; the result revealed that the crystallinity of the neat Polypropylene decreased with increasing filler loading and the compatibility of phases were adequate.

Also Sumari et al, 2013, studied the effect of ultrasound treatment on the morphology, particle size crystallinity, and crystallite size of cellulose and showed morphological breakdown with increase in ultrasound. Other researched works on modification of basic mechanical properties through carbonization are that of Momoh et al, 2016 and Ayo et al, 2011.

The present study report the modification of coconut shell powder through carbonization and its application in rubber reinforcement and development. Scanning electron microscopy and X-ray diffraction were done. Mechanical and chemical properties of the composites were also evaluated.

II. MATERIALS AND METHODS

MATERIALS

Coconut shell wastes were found in Auchi, Edo State (Nigeria) and its environs. The natural rubber (Standard Africa Rubber, SAR3) was the grade used. Compounding additives: Zinc oxide, Stearic acid, Sulphur, MBTS, TMTD and Mineral oil were of commercial grades.

PREPARATION OF THE SHELL AND CARBONIZATION

The coconut shell was collected, washed in water to remove sand and debris, and then oven- dried at 95^0C for 1 hour to remove moisture. 5 portions of 200g of the dried portion were carbonized at 300, 400, 500, 600 and 700^0C for 3 hours each (Ayo et al, 2011). The 5 carbonized portions and a raw portion were ground using a grinding mill to fine powder from which 100µm particle sizes were characterized using standard methods prior to compounding.

COMPOUNDING AND CURING

A laboratory two-roll mill (180 x 360mm) was used for the homogenization and mixing in accordance with ASTM – D3182. The nip gap, mill roll speed ratio of 1:1.25, sequence of addition and time of mixing of the additives were held uniform for the entire composite samples. The temperatures of rolls were maintained at 70^0C. Maturation for 24hours at 32^0C was allowed for the selected compounds before press curing in accordance to ASTM – 1632-07. A compression pressure of 150kg/cm^2, temperature of 150^0C and a time of 15minutes were used as determined from ODR 2000 Model Rheometer.

MORPHOLOGICAL EVALUATION

Micro structural analysis was performed using a Scanning Electron Microscope (FEI Inspect S-50 that using data analysis software server XT microscope). SEM magnification was at 1000X with a resolution of 80µm. The sample surfaces were coated with a thin layer of gold using a Bal-Tec SCD 005 sputter coater to provide electric conductivity. Secondary electron mode at a 10kv mapping acceleration voltage with full BSD was used. Particle properties were measured by volume and count using particle size analyzer (Beckmann Coulter L5 200). SEM images of the raw and carbonized coconut shell powder (CSP) at the various temperatures are indicated in figure 1.

X-RAY DIFFRACTION MEASUREMENT

X-ray diffractograms were collected using a sample holder mounted on a Shimadzu Diffractometer (XRD 6000), with monochromatic CuKα radiation (λ = 0.1542nm), the generator operating at 40Kv and 30mA. Intensities were measured in the range of $2 < 2\theta < 60^0$, typically with scan steps of 0.3^0 and 6^0min^{-1}. Peak separations were carried out using Gaussian deconvolution. After deconvolution it was possible to calculate and compare several parameters. The d-spacings were calculated using the Bragg's equation (Newman, 1999 and Newman, 2008). The average size of crystallites, Bhkl was estimated from the widths of reflection hkl, using the well-known formula of Scherrer (Popescu et al, 2011). See diffractograms of raw and carbonized coconut shell powder at 500^0C in figure 2 and percentage crystalline index in table 1.

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MECHANICAL EVALUATION

The following tests were further conducted as confirmatory tests on the compounded composites using standard test methods. Hardness (ASTM -D2240), Abrasion resistance (ASTM-D5963-04), Compressive strength (ASTM-D575-91), Tensile strength, Modulus, Elongation at break and Flexural tests (ASTM-D3039/D). All measured properties were along the grain direction. Results are shown in table 2.

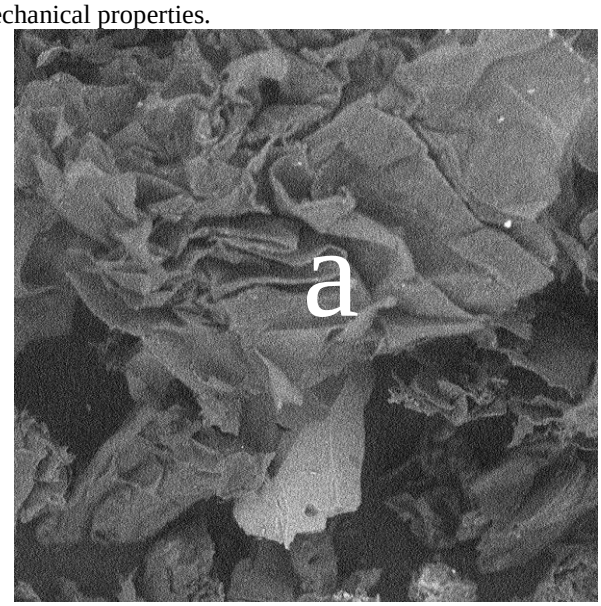
CHEMICAL EVALUATION

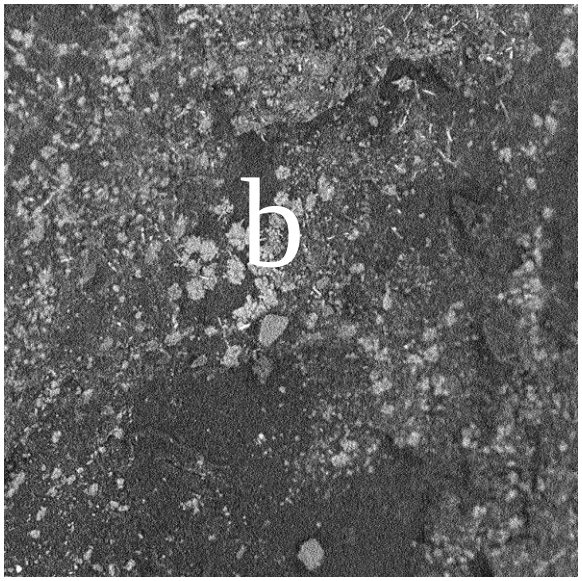
Vulcanized compositions were obtained as small sheets of about 1.5g and approximately ($2\times2\times 0.3$) cm in accordance to ASTM-D 3010. The exact weights of dry sample were measured prior and after immersion in the selected solvents for 72 hours at temperature of 35^0C. The equilibrium swelling of the compounds in percentage were mathematically gotten using 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. Results of swollen test are depicted in table 3.

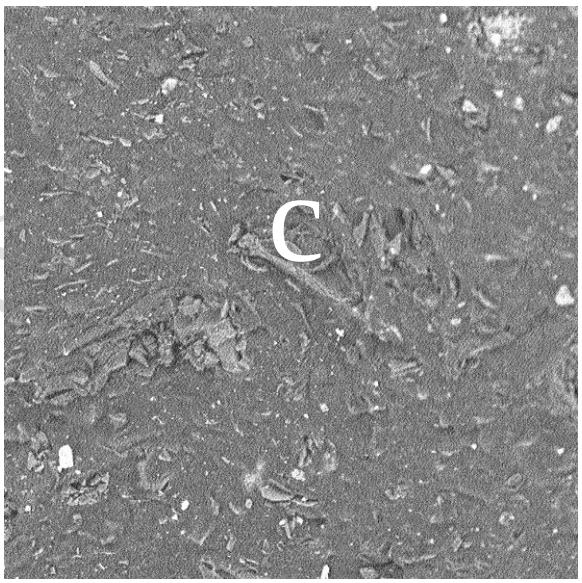
III. RESULTS AND DISCUSSION

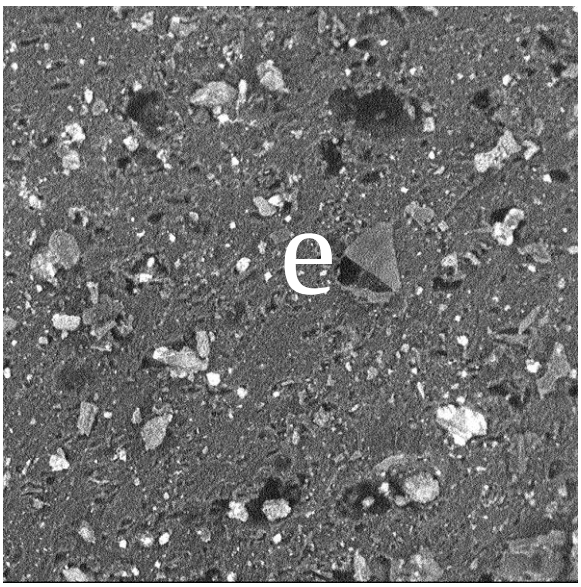
MORPHOLOGICAL EXAMINATION

It could be seen that as carbonization temperatures increase, the surface of the powder gets finer, clearer and an obvious optical clarity with the presence of tiny-like shinning particles could be observed. Darker stacked arrangements of aggregated particles are visible. The tiny glassy- like particles suggests regular arrangements, properly aligned morphologies and structure which could have resulted from modification. The more glassy and structured the particles are the better the interfacial interactions between filler and the rubber compound (Eiras and Pessan, 2009). The agglomerated areas create stress concentration zones which might act as a hardness initiator and therefore leading to reinforcement in mechanical properties.









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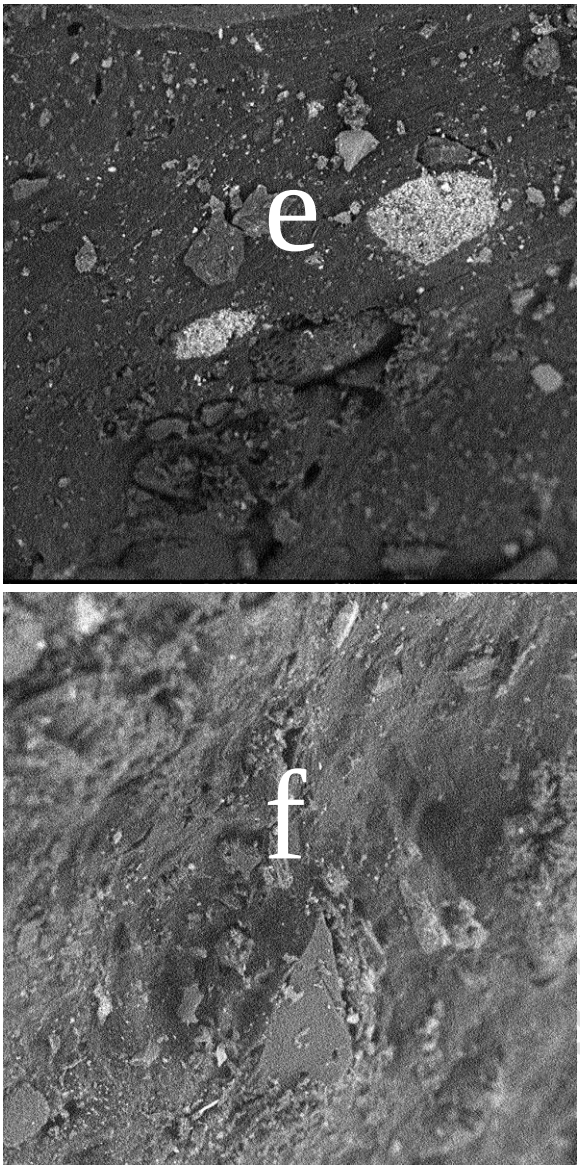

Figure 1: Morphologies of CSP at (a) raw powder, (b) 300, (c) 400, (d) 500, (e) 600 and (f) 700^{0}C

X - RAY DIFFRACTION

As mathematically indicated in table 1 using a combination of the Bragg's Law (Eq. (1)) and Scherrer equation (Eq. (2)) the d-spacing, crystalline index and crystallite sizes (Newman, 1999, 2008 and Popescu et, al, 2011) Percentage crystallization were obtained from the diffractograms.

$$C.I = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad 1$$

Where, I_{002} and I_{am} are the intensities of the crystalline and amorphous regions. The apparent crystallite size (L) (Eq. (2)) was calculated using the Scherrer equation (Popescu et al, 2011):

$$L = \frac{k\ \lambda}{\beta\ \cos\theta} \quad 2$$

Where K is a constant of value 0.9, λ is the X- ray wavelength (0.1542nm), β is the half-height width of the diffraction band and θ is the Bragg angle corresponding to the (200) plane.

Parameter for XRD	CSP	300	400	500	600	700
Crystallinity (%)	60.2	71.2	82.9	87.7	86.2	85.6
ACD (A^0)	≈3.7	≈3.7	≈3.7	≈3.7	≈3.7	≈3.7
Intensity Counts	44	52	72	87	85	84
FWHM	0.20150	0.16520	0.16000	0.15970	0.15180	0.11820
2θMaximum Peak	21.0759	22.0779	23.0465	24.9875	23.9441	23.0689

Table 1: Crystalline Parameters

From table 1 above, as carbonization temperatures increase, the amorphous regions tend to diminish compared to the stability of the crystalline region. As the amorphous region diminishes, the more stable crystalline region becomes more intensified, thereby leading to increase in percentage crystallinity (Popescu et al, 2011). The Average Crystalline Dimensions (ACD) are averagely the same possibly as the particle size of the powder were all at 100µm. Intensity counts increases with carbonization temperature leading to more crystalline region up to the 500^{0}C. Full width at half Maximum (FWHM) decreases with carbonization temperature thereby reducing the d-spacing between particles and improvement on Crystallinity. The Bragg's angle (2θ) peaked within narrow range of values for the temperatures used; possibly around the characteristic peak value for the coconut shell (Ismail et al, 2002). Increase in the percentage of crystallinity will increase the mechanical, chemical, optical and thermal properties of the coconut shell powder and consequently an indicative increase in the reinforcement properties of the composites (Eiras and Pessan, 2009; Joseph et al, 2003). Also see the diffractogrames of raw and at 500^{0}C carbonization treatment in figures 2 (a) and (b) below.

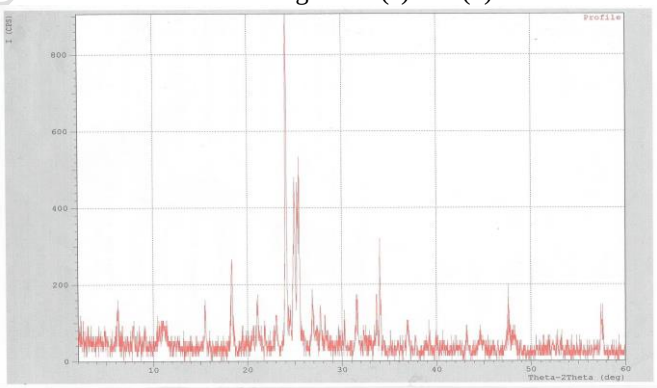

Figure 2 (a): X-ray Diffractogram of Raw Coconut Shell Powder

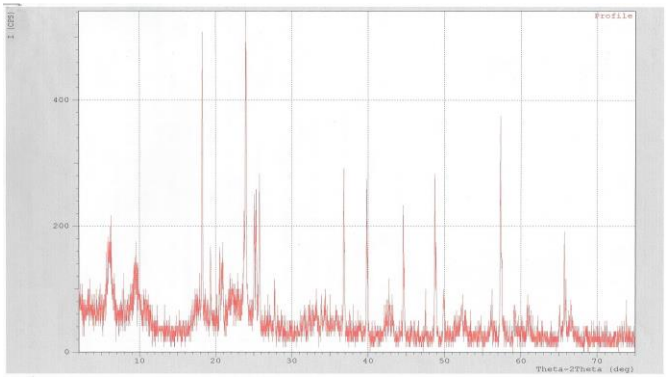

Figure 2 (b): X-ray Diffractogram of Carbonized Coconut Shell Powder at Best Temperature of 500^{o}C

MECHANICAL PROPERTIES

The results of the mechanical properties confirmed increase in hardness, abrasion resistance, tensile strength and modulus up to carbonization temperature of 500^0C. Possibly as a result of greater reactivity between the filler and the rubber matrix (Ayo et al, 2011). These clear increases will definitely lead to increase in composites reinforcement.

The values of elongation at break and compression set decrease with increase in carbonization temperature possibly due to the adherence of the filler to the polymer chain. The stiffening of the chain leads to high resistance to stretch when the strain is applied (Onyeagoro, 2012). Basic mechanical properties started decreasing at carbonization temperatures above 500^0C. See results on table 2 below.

Properties	CSP	300	400	500	600	700
Hardness (Shore A)	73.00	75.00	78.00	86.00	80.00	76.00
Abrasion Resistance	22.51	28.42	32.10	36.90	44.84	37.42
Compression set (%)	28.90	26.40	24.80	22.30	23.00	23.20
Tensile Strength (MPa)	3.91	4.21	4.30	5.20	4.90	4.80
Elongation @ Break (%)	494.50	484.60	420.00	398.20	395.00	398.20
Modulus (%)	1.92	3.10	4.35	5.40	5.38	5.12
Flexural Strength (MPa)	0.99	0.39	0.28	0.46	0.38	0.21

Table 2: Mechanical Properties of the Composites

CHEMICAL TESTS

With increase in carbonization temperature, the rubber compound develops more resistance to solvent swelling. The possible reason is the increase in crosslink formation and density as carbonization temperature increased (Momoh et al, 2016). The molecular chain gets stiffer and become more firmly bonded together. See table 3 below.

Carbonization Temperature (°C)	Hexane	Xylene	Toluene	Benzene
Raw CSP (32°C)	425	400	402	248
300°C	394	385	394	240
400°C	342	372	368	230
500°C	274	281	300	228
600°C	236	240	256	222
700°C	221	218	248	200

Table 3: Chemical Sorption Test Results

IV. CONCLUSION

Modification through carbonization diminished the amorphous region and intensified the crystalline region of the coconut shell powder. Morphological examinations also indicates finer and clearer particle aggregates and hence an improvement in filler-matrix interactions and reinforcements. Increase in finer particle aggregates, intensification of the crystalline region and decrease in crystallite size of the coconut shell powder became pronounced with increase in carbonization temperature. There was a noticeable reduction of the full width at half maximum (FWHM) of the X-ray diffractograms, but the d-spacing were averagely the same.

However, the highest crystallinity and morphological built up occurred at the 500^0C of carbonization. Chemical and mechanical properties of hardness, tensile strength, abrasion resistance, and modulus were also more pronounced at 500^0C of carbonization. The inference here is that carbonization of the coconut shell powder has a major effect on the crystalline intensity, morphological outlook, chemical disposition and mechanical properties of the natural rubber composites. These observed positive effects lead to appreciable reinforcement and therefore recommendable and significant to the development of engineering products from natural rubber filled with carbonized coconut shell filler.

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