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ENHANCEMENT OF MECHANICAL, WEAR AND WATER ABSORPTION PROPERTIES OF CHICKEN FEATHER FIBRE REINFORCED NATURAL RUBBER VULCANIZATES VIA ALKALINE TREATMENT

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Abstract: Limitations of keratin based fillers amongst other organic fillers generally include high moisture absorption, relatively low strength and poor dispersion in matrix. Therefore, several surface treatment methods are employed in order to enhance fibre hydrophobicity, roughness, wettability, interfacial adhesion and dispersion. In this study, chicken feather fibres were stripped off their quills and pretreated with 0.25M of sodium hydroxide solution for 4 h at 50°C and size reduced. The morphological changes were observed via Scanning Electron Microscopy (SEM). Thereafter, natural rubber (NR) vulcanizates were developed with untreated versus treated chicken feather fibres as fillers using a two roll mill and a compression moulding machine. The effect of treatment and varying filler loading (from 0 to 10 ppH) on the water absorption, wear and mechanical properties: tensile strength, elongation at break, modulus (M300) and energy at break were studied. Tensile strength, M300, elongation at break and energy at break were enhanced from 2.52 to 3.84 MPa, 2.02 to 2.10 MPa, 485 to 608% and 5.5 to 16.44 J, respectively. Wear rate and water absorption rate reduced from 0.4 to 0.18% and from 1.9 to 1.3%, respectively. Alkali treatment thus enhanced the reinforcement and abrasion resistance properties of feathers in natural rubber vulcanizates.

Keywords: Feather fibres, sodium hydroxide, SEM, tensile test, vulcanizates, wear

Introduction

Feathers are the integuments of vertebrate animals that are structurally capable of transferring forces without significant changes. They are a rich source of about 91% β-keratin, 8% lipids and 1% water which is an insoluble fibrous protein (Khosa *et al*., 2013). Their fibres possess higher aspect ratio than the quill which translates to higher mechanical strength (Oladele *et al*., 2015). When used as fillers in composite development, feathers have been reported to improve biodegradability and biocompatibility (Ntumba and Prochon, 2016); thermal insulation and stability (Flores-Hernandez, 2014); tensile strength (Adetola *et al*., 2014); hydrophobicity (Acda, 2010) and modulus (Barone and Schmidt, 2005) amongst other property enhancements.

Nevertheless, chicken feather fibres (CFF) can be surface modified to enhance tensile properties, abrasive resistance, rub resistance, oil and water repellency (Hu *et al*., 2011). Amongst several surface modification techniques, alkali treatment (mercerization) is reported to be cost effective, available and capable of improving the structural integrity of keratin structures without deteriorating their intrinsic properties (Oladele *et al*,. 2015). Hashim *et al*. (2012) also reported that mercerization sufficiently removes wax and alters some hygroscopic amino acids which enhances surface roughness, increases reactive sites and hydrophobicity.

Several authors have treated chicken feather fibres with potassium hydroxide (Okoro *et al*., 2016); potassium hydroxide/ sodium hydroxide/ hydrogen peroxide (Oladele, 2016); sodium hydroxide (Oladele *et al*., 2013) and sodium hydroxide/maleinized polybutadiene rubber/silane coupling agent (Huda *et al*., 2012). Oladele (2016) compared the effect of potassium hydroxide, sodium hydroxide and hydrogen peroxide in the pretreatment of feathers and reported that sodium hydroxide was cheaper, relatively available and yielded better enhancements. Ghani *et al*. (2014) studied the effect of sodium hydroxide treatment on some mechanical properties of LDPE/Chicken feather fibre composite. From their results, higher tensile strength, Young's modulus and final decomposition temperature (as revealed by Thermogravimetric analysis) were enhanced while mass swell percentage decreased.

Natural rubber (cis-1, 4-polyisoprene) is not suitable for engineering applications in its unprocessed state due to lack of strength properties and vulnerability to wear and degradation. Thus, it is cross-linked with vulcanizing agents and reinforcing fillers. A few works have reported the use of chicken feathers as fillers for rubber composite development enhancement in static and dynamic mechanical properties (Mendez-Hernandez *et al*., 2018; Hergenrother *et al*., 2105).

This study was aimed at investigating several property enhancements brought about by the alkali treatment (sodium hydroxide) of chicken feather fibres size using a top-down approach and compounded as filler to produce rubber vulcanizates.

Materials and Methods

Materials

Chicken feathers were collected from a slaughter house in Sabon-gari Local Government Area, Zaria, Nigeria. Sodium hydroxide (analytical grade) was procured from Cardinal Lab and Chemical Supplies, Hanwa Zaria, Nigeria. Natural rubber (dry crumb) and other vulcanizing agents were procured from Tony West Rubber factory, Lagos Nigeria. The rubber specifications were: ≤ 0.05% dirt content, ≤ 1.00% volatile content, ≤ 0.7% nitrogen content, ≤ 0.6% ash content, minimum of 30 initial plasticity, minimum of 60 plasticity retention index (PRI) and blackish brown colour.

Preparation of treated and untreated feather particles

The chicken feather fibres were stripped off their quill, washed and sun dried. They were further subjected to alkali treatment in a water bath with 0.25 M of sodium hydroxide solution for 4 h at 50°C. The treated fibres were thoroughly washed with distilled water till they were neutral in pH and oven dried at 80°C for 2 h. The dried treated and untreated fibres were then size reduced in a Thomas-Wiley laboratory mill through 0.05 mm mesh sieve. The particles obtained were further ball milled at an estimated vessel speed of 300 rpm at ball to particle ratio (BTP) of 1: 20 on weight basis for several hours. The ball milled feather fiber attained 80% size distribution between 38.4 – 282.9 nm as revealed by Dynamic Light Scattering (DLS) method with the aid of Malvern mastersizer 3000 (Malvern instrument UK) using water as the dispersant at viscosity of 0.8872 Cp.

Compounding of composites

Treated and untreated feather fibres, vulcanizing agents and natural rubber as the matrix were mixed using a two roll mill, followed by vulcanization in a compression moulding machine at 140°C for 13 min. Table 1 shows the formulation used for compounding.

Table 1: Formulation of rubber composite

Ingredients	Parts per hundred (ppH)
Natural rubber	100
Stearic Acid	2
Zinc oxide	5
Sulphur	3
Mercaptobenzothiazole	2
Trimethyl quinolone	1
Fillers (treated and untreated particulate feathers)	0 – 10 (at an interval of 2)

Tensile properties (tensile strength, elongation at break and modulus 300% and energy at break)

The American Society for Testing Materials ASTM D3184-89 Standard was used to formulate rubber composites. Dumbbell shaped samples were made and used to carry out tensile analyses in accordance with ASTM D412. The maximum breaking stress (tensile strength, σ_t) was calculated using the equation below:

$$\sigma_t = Fbd$$

Where F is breaking force (N), b is the width (mm) of the sample and d is the thickness (mm) of sample.

Elongation at break was calculated according to the equation below:

$$Elongation\ at\ break = \frac{Final\ length\ at\ fracture - Initial\ guage\ length}{Initial\ guage\ length} \times 100\%$$

Similarly, the modulus at fracture was calculated using the equation below:

$$Elastic\ modulus = \frac{Maximum\ stress\ at\ break}{Strain\ at\ break}$$

$$Modulus\ at\ 300\%\ elongation = Stress\ at\ 300\%\ elongation$$

Energy at break was electronically determined by the Universal Tensile Testing Machine.

Water absorption rate

Vulcanized samples were cut out in spheres with a constant diameter of 20 mm and thickness of 4 mm from each formulation. The samples were oven dried to constant weight and immersed in distilled water in air tight containers for 48 h at room temperature (32°C). They were then removed and dried with a lint-free cloth. The weight before immersion (a_1) and after immersion (a_2) were taken and recorded. Samples were subjected to water absorption test in triplicates and an average taken. The rate of water absorption (A %) was measured using the equation below.

$$A\ \% = \frac{a_2 - a_1}{a_1} \times 100\%$$

Wear test

The abrasion loss of the vulcanized rubber composite samples were determined with the aid of rotary drum abrader in terms of volume loss according to ISO 4649 – 2010 (E) standard using a Martindale Abrasion machine. Three abrasion specimens of each sample with thickness 5 mm and diameter 30 mm were prepared with a drill. The samples were removed from a dessicator and weighed before the procedure. Each sample was mounted against the drum of the abrasion testing machine at applied force of 10 N. The abrasive surface of the wear test machine was covered with an abrasive paper of grade P 220. The machine was programmed to run and stop after 100 revolutions at 40 rev/min. The samples were reweighed at the completion of each run. The initial, w_1 and final weights, w_2 of the samples in triplicate were measured and the mean weight losses calculated according to equation below.

$$W\ \% = \frac{w_2 - w_1}{w_1} \times 100\ \%$$

The effect of varying filler loading and filler type on weight loss of natural rubber composites were plotted as shown in Fig. 5.

Results and Discussion

SEM analysis

Scanning electron microscopy was used to view the feather fibres prior to and after alkali treatment which are shown in Plates I and II, respectively.

Plate I: SEM graph of untreated feathers at 350x (760 µm)

Plate II: SEM graph of treated feathers at 350x (760 µm)

From the micrographs (Plates I and II), waxy outer layers of the feather fibres were stripped off by the alkali treatment. This is akin to Sardauna *et al*. (2011) whoreported removal of the membrane layer that covered the outer surface of hemp fibres when treated with sodium hydroxide as revealed by SEM. The untreated fibers looked waxy compared to their treated counterpart in topography as reported by Hashim *et al*. (2012). Strands of slimmer fibres were also observed from the treated micrograph in Plate II which was attributed to the removal of waxes as reported by Oladele *et al*. (2018); Aly *et al*. (2012) and Ku *et al*. (2011).

Tensile strength

The tensile strength analysis reveals the load bearing capacity of the composite samples. The tensile strength values of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (TF and UF) at varying filler loadings were shown in Fig. 1.

From Fig. 1, there was an increasing trend observed when the vulcanizates were filled with both untreated and treated feathers. This shows that feather fibre exhibited good reinforcement abilities and has good interfacial adhesion with rubber as matrix. However, upon treatment the filled vulcanizates yielded higher tensile strength. This was akin to the work reported by Oladele *et al*. (2018), where treated chicken feather fibres were used as reinfrocement in HDPE. Highest tensile strength values were recorded at filler loading of 10 ppH. Tensile strength enhancement of 52% was achieved by the alkaline treatment.

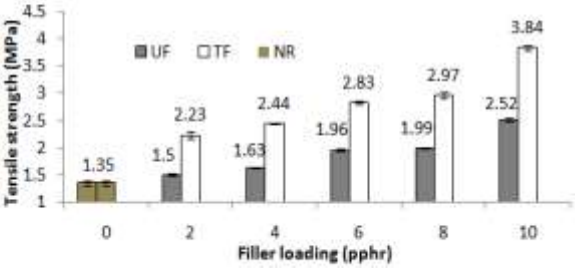

Fig. 1: Tensile strength values for rubber vulcanizates reinfoced with treated and untreated feathers

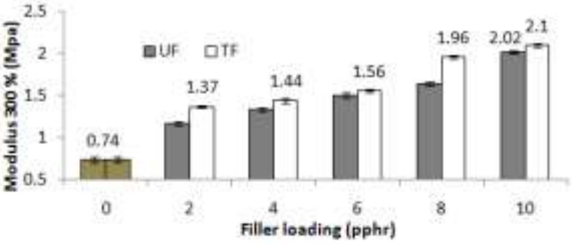

Fig. 2: Modulus 300% for rubber vulcanizates reinfoced with treated and untreated feathers

Modulus 300%

The modulus corroborates the stiffness of the material. The modulus at 300% elongation for the was obtained from the rubber vulcanizates stress-strain curves in Appendix A. The modulus 300% values of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (TF and UF) at varying filler loadings were shown in Fig. 2.

From Fig. 2, fillers generally enhanced modulus compared to the unfilled/neat rubber vulcanizate at 0.74 MPa. The modulus of both treated and untreated filled vulcanizates significantly increased as filler loading increased. Nevertheless, treatment enhanced the stiffness of the filler and consequently the modulus of the rubber vulcanizates. Highest values were obtained at 10 ppH with untreated filled vulcanizate at 2.02 MPa and filled vulcanizate at 2.10 MPa. This is akin to the work by Ghani *et al*. (2014)who reported enhanced the mechanical properties (tensile strength and modulus) of LDPE/Chicken feather fibre composite when the feather fibre was treated with sodium hydroxide.

Elongation at break

Elongation at break relates to the stretching limits of the composite. Generally, incorporation of fillers tend to reduce the elasticity of rubber chains corroborating a decrease in elongation. The elongation at break values of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (TF and UF) at varying filler loadings was shown in Fig. 3.

From Fig. 3, a general decrease in elongation at break was observed with unfilled and filled rubber vulcanizates. This decrease in rubber chain elasticity is expected with the addition of fillers (Aguele *et al*., 2012). Nevertheless, untreated fillers exhibited more rigidity as the elongation at break was less than that of treated feather vulcanizates. Rubber vulcanizates with treated fillers showed general increase in elongation at break up to 8 ppH. Rubber vulcanizates with untreated fillers at 2 ppH alone yielded higher elongation at break than the vulcanizates with treated fillersbut generally showed a decreasing trend in elongation from 2 to 10 ppH. Therefore, treated filled vulcanizates can be better suited for end products where elasticity is required.

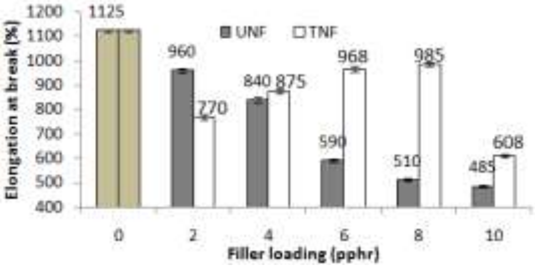

Fig. 3: Elongation at break values for rubber vulcanizates reinfoced with treated and untreated feathers

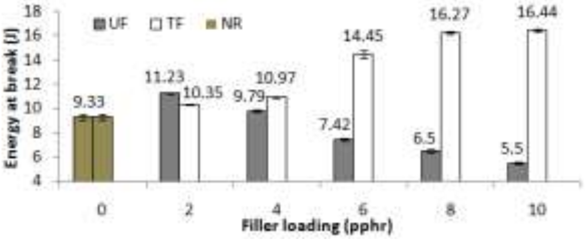

Fig. 4: Energy at breakvalues for rubber vulcanizates reinforced with treated and untreated feathers

Energy at break

The values for energy absorbed by the vulcanizates at the point of fracture of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (UF and TF) at varying filler loadings and type was shown in Fig. 4. It corroborates the amount of work done to break the bonds or fracture the vulcanisates.

Keratinous fillers are reported to display unique viscoelastic behavior which makes them capable of absorbing energy (Wang *et al*., 2016). From the Fig. 4, energy at break increased as the filler loading increased only for the treated fillers . The energy at break was only higher for the untreated at 2 ppH with a value of 11.23 J. At 10 ppH, energy at break was enhanced by the treatment from 5.5 to 16.44 J. The energy at break or fracture is attributed to the toughness of the reinforcing filler. This imples that alkali treatment enhanced the toughness of the fibres and overall composite. It also implies that the bonds formed between the treated fibre and the matrix are stronger. The high disparity of 199% observed at 10 ppH in energy at break values was attributed to low interaction between untreated fillers and their matrix as compared to their treated counterpart.

Wear

Abrasive wear is the removal of material due to penetration of hard particles or contact with the surface of a body in sliding contact. Wear in natural composite development yield products with low use and economic value (Verma *et al*., 2014). The wear rate values of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (TF and UF) at varying filler loadings were plotted in Fig. 5.

A reduction in wear rate can be explained by better filler dispersion and adhesive strength between filler and matrix (Aguele *et al*., 2014). Generally, the fillers improved on abrasion resistance of the rubber matrix which implies that wear rate of both untreated and treated feather reinforced vulcanizates were seen to reduce as filler loading increased. This was due to better adhesion and interaction between feather particles and the rubber matrix. Nevertheless, the alkali treatment further improved the wear rate from 0.4 to 0.18% at 10 ppHas a result of enhanced surface roughness. This corroborated studies by Shalwan and Yousif (2013) and Uzun *et al*. (2011), who reported an improvement in wear resistance upon alkaline treatment of natural fibres.

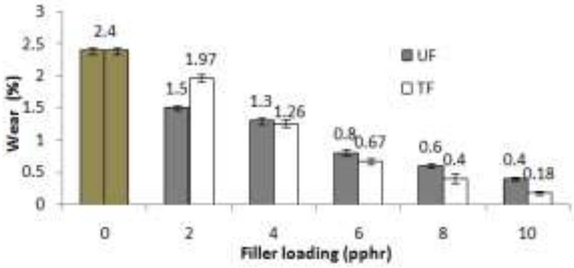

Fig. 5: Wear percent for rubber vulcanizates with untreated and treated feather

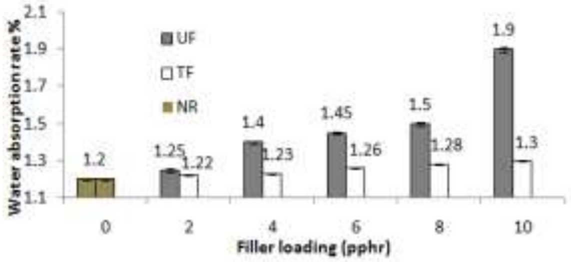

Fig. 6: Water absorption rates for rubber vulcanizates reinfoced with treated and untreated feathers

Water Absorption Rate

Water absorption tendencies in a polymer composite connote its performance under service conditions and its degradability. The water absorption rates of neat rubber vulcanizates (NR) and rubber vulcanizates when filled with treated and untreated feathers (TF and UF) at varying filler loadings were shown in Fig. 6.

From Fig. 6, the filled rubber vulcanizates generally exhibited an increment in water absorption rate compared to unfilled/neat rubber vulcanizates. Also, water absorption rate continued to increase for rubber vulcanizates filled both with treated and untreated feathers. This was attributed to the partial hygroscopic nature of the feather fillers. Nevertheless, the vulcanizates with untreated fillers exhibited greater water absorption rate than vulcanizates with treated fillers. At 10 ppH, vulcanizates with untreated fillers had a water absorption rate of 1.9% as against 1.3% for vulcanizates with treated fillers. This shows that the treatment was able to reduce the hygroscopic amino acids inherent in feather keratin. This was similar to the report by Oladele *et al*. (2018). It also showed that better crosslinks were formed by the treated fillers which created an immobilization of the polymer chains to a certain degree improving water resistance. This is akin to the work by Chigondo *et al*. (2013).

Conclusion

Sodium hydroxide treatment was shown to be effective in the surface modification of chicken feather fibres and its enhancement for reinforcement in natural rubber vulcanizates. From this study, Tensile strength, M300, elongation at break and energy at break were enhanced from 2.52 to 3.84 MPa, 2.02 to 2.10 MPa, 485 to 608% and 5.5 to 16.44, J, respectively. Wear rate and water absorption rate decreased favourably from 0.4 to 0.18% and from 1.9 to 1.3%, respectively. The developed rubber vulcanizates can find possible applications in the production of footwear, floorings and flexible toys.

Recommendations

Further study to improve on reinforcement ability of feathers should be investigated. Thereafter, other properties should be analyzed and the effect of higher filler loadings studied to determine its suitability over a wide range of end applications.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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