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Original Research Article

Mechanical and chemical properties of selected mullusc shells in Nigeria

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Important mullusc shells in Nigeria include those of land and water snails, the periwinkle and the clam. Some farmers burn them to reduce crushing strengths before grinding for livestock feeds as a source of calcium and other mineral elements. They are also said to be a good liming material for acid soils. It is believed that burning may destroy some of these elements. This work was to investigate their mechanical and chemical properties which may help in the development of affordable equipment to crush the shells without burning. The shells were selected according to size range and subjected to size measurements in terms of equivalent diameter, D_e, sphericity, ϕ, and aspect ratio. The sphericity and aspect ratio of the shells of water snail, the clam and the periwinkle were almost constant, the size notwithstanding. The crushing strengths for all the size range of the shells were determined. Other physical properties such as true density, ρ_t, bulk density, ρ_w, porosity, angle of repose, coefficient of static friction on different surfaces, for the ground materials, were investigated. Chemical analysis showed that clam shell was the richest in calcium, sodium, potassium and phosphorus.

Key words: Mollusk shells, size range, size measurement , aspect ratio, crushing strengths, density, coefficient of static friction, micronutrient elements

INTRODUCTION

Molluscs or Mollusks are of the phylum, Mollusca, a large group of invertebrate animals. They form the largest marine phylum. A lot of them also live in fresh water and terrestrial habitats. Molluscs are highly diverse in size, anatomical structure as well as in behavior and habitat (Morton,19979; Wikipedia,2009). Molluscs are characterized by a soft body, usually with an exoskeleton in the form of a shell. They consist of a body, a single muscular foot, a dorsal mass with a visceral sac and flesh skin fold(Purchon,1977).The shells provide protection for the soft-bodied inhabitants against predators (Kaplan,1998). Still other molluscs such as the octopus, squid, and the sea slug have no external shells but they evolve their own survival strategies, for example, having complex brain to replace their protective armour (Sea and Sky, 2000).

Molluscs are classified into groups or orders. The snails belong to the order, Gastropoda. They have one shell(univalves) It is this shell that makes some of them popular ocean treasures as they display more diversity and beauty than any other ocean treasure (Sea and Sky,2000). Another group(order Bivalvia), known as the bivalves have two shells. They include the clams, scallops and oysters. It is the oyster that is used in producing the most coveted of the ocean's treasures, the pearl, the mother pearl (Wikipedia,2009). Yet another group (order Cephalapoda), is that of the mollusks without exoskeleton. They include the octopus, squid and the seaslugs (Salvini-Plawen, 2014).

The shells are formed by limey secretions from a tiny

Figure 1: land snails

coral polyp (mantle) at the dorsal part of the body. The secretions, consisting of inorganic substances, harden into coral structure. The substances making up this shell are mainly chitin and conchiolin which consist of protein hardened with calcium carbonate as well with a variety of mineral salts (Lambert, 1973; Bowen, 1996)

There are two forms of calcium carbonate, aragonite and calcite. Their crystal shape differs but the chemical formula is the same. Aragonite is the denser form and is found in the hard or scleractinian corals. Aragonite or calcite can be formed depending on the seed crystal' growth pattern and the proteins secreted by the polyps. If both polymorphs are present in a particular shell, they are typically separated in different layers (Keeney and Corey,1963; Tompa, 1976). Most mollusk shells are composed mainly of aragonite. However, those of gastropods that lay eggs with hard shells use calcite(sometimes with traces of aragonite) to construct the eggshell.

Because Oyster shells and other sea-shells are largely of calcium carbonate, they can be used to increase soil pH (Akpabio, 2006). The effectiveness of raising soil pH depends on the degree of fineness to which they are crushed. The finer the particles the greater is this effectiveness because of greater surface area for reaction. The calcium (Ca) in the form of silicates may have value primarily as a liming material and can correct acidity. Pearson and Adams (1967) stated that when mollusc shell is added to an acid soil, the calcium silicate contained in it neutralizes soil acidity in the manner similar to that of limestone.

Calcium is one of the most abundant elements in the body (man and animal), and it is often the major cation in the diet (Whitney and Rolfes, 1996). More than 90% of the body's calcium is in the skeleton, bones and teeth. Calcium is also important in cellular metabolism, blood clotting, enzyme activation and neuromuscular action. It is also very important for egg shell formation and milk secretion. Therefore calcium supply is very important in the nutrition of man and animal.

Different products are used worldwide to provide calcium for poultry and other livestock feeds. Calcium carbonate (limestone) is the most common source. Other sources of concentrated calcium include ground oyster shells, snail shell, other marine shells (Gregor,1998). There are certain considerations for the selection of calcium source for animal feeds. They include: (i) calcium content to meet the requirement of the specie of animal, (ii) ability to blend with other feed ingredients, and others. McNaughton, et al.,(1974)), demonstrated that calcium utilization from oyster shell and limestone by chick was dependent upon the particle size of the supplement. They preferred the use of a medium to fine particle size calcium supplement in the diet.

It is obvious that any calcium product which is to be utilized for either soil treatment or feed preparation, must be crushed into tiny particle sizes. Therefore the study of the mechanical, physical and chemical properties of these products is very important for the development of crushing and handling equipment for them.

Major local mulluscs are the land snail (Figure 1), the water snail (Figure 2), the periwinkle (Figure 3), and the clam(Figure 4). The first three are univalves while the clam is a bivalve. They are in the daily diets of most homes in the South-Eastern part of Nigeria. The periwinkle is the most abundant and is available throughout the year. It comes from both marine and brakish (mixture of fresh and salt waters) waters. The clam is found in the brakish water, deep in the river bed. It is seasonal. The specie of clam used for this work is not common in Nigerian waters. It is found only in the brakish section of Cross river in the South-Eastern part of Nigeria. Others are the land snail, found in bushes and forests and the water snail, found in the banks of streams and rivers. The shells of these mollusks are in large quantities for crushing for use in feeds and soil

Figure 2: Water snails

Figure 3: Periwinkles

Figure 4: Clams

amendments local feeds producers utilize these shells, especially the hard ones (from periwinkle and clam) as a source of calcium for their feeds. The shells are often burnt to reduce crushing strength before they are ground into fine particles. Subjecting them to very high temperatures during burning may destroy nutrient elements and minerals contained in them, hence the need to develop small scale affordable crushers to crush the shells without first burning them. The agricultural soils of Southern Nigeria are poor and acidic on account of heavy rainfalls and erosion activities. Availability of the crushed shells will help in liming the soils for higher agricultural productivity.

The objective of this work was to determine mechanical and chemical properties of these important mullusc shells in Nigeria for their possible exploitation.

MATERIALS AND METHODS

Materials

Fresh mollusc shells of periwinkle, clam, land snail and water snail were selected according to size range, the large, medium and small. The samples so collected were oven dried at temperature of 40°C to reduce the moisture content but not to destroy the chemical contents.

Limestone (calcium carbonate) was brought in as a reference material.

Determination of Mechanical/Physical Properties

Size Measurements

Linear dimensions, length (L) width (W) and thickness (T), were measured with digital vernier caliper. The size of the materials indicated by equivalent diameter, D_e, sphericity ϕ, and aspect ratio, were determined by the following relationships (Gupta and Das, 1997; Joshi, Das and Mukherjee, 2003; Faleye and Atere,2009).

$$D_e = (LWT)^{1/3} \qquad (1)$$

$$\varnothing = \frac{D_e}{L} \qquad (2)$$

$$Aspect\ ratio = \frac{W}{L} \qquad (3)$$

Surface area

The surface area, A (cm^2) was determined by placing the sample on a graph sheet and tracing its outline with a sharp pencil and the area estimated by the number of square (Ogunsina et al., 2009). Many replicates of the same size range were made and the average value determined.

Crushing Strength

Samples were crushed in a 250kN digital crushing machine, GIMAX3 compression Chi. Maximum crushing load, L (kN) was indicated on the machine. This was also shown graphically on the machine as the elastic limit of the material (Fellows, 2003). The crushing strength was determined by the ratio of the crushing load to the surface area (Poulsen,1978; Olalusi et al,2009).

Thus crushing strength

$$S = L\,/A \quad N/mm^2 \qquad (4)$$

Density Determination, ρ

True density, ρ_t, and bulk density ρ_b of the ground materials were determined.

True Density, ρ_t, by water displacement

The sample of the ground material was weighed in air with mass, M_a, and emptied into a graduated cylinder containing water. The mass of water displaced by the material was recorded as M_w. This was repeated 3 times and average value found. True density was calculated from the expression.

$$\rho_t = \left(\frac{M_a}{M_a - M_w}\right)\rho_w \qquad (5)$$

Where $\rho_w = density\ of\ water$

Bulk Density, ρ_b

The ground material was weighed and recorded as M, and emptied from a constant height into a graduated cylinder, a container of known volume, V, (AOAC, 1984; Ogunsina et al., 2009). Bulk density is given by:

$$\rho_b = \frac{M}{V} \qquad (6)$$

Porosity or Packing Factor (PF)

Determined by the expression given below (Mohesenin, 1986)

$$PF = 100\left(1 - \frac{\rho_b}{\rho_t}\right) \qquad (7)$$

Static Angle of Repose

A cylindrical container open at both ends was placed on a flat surface, and filled from the top with the ground material. The cylinder was lifted up gradually, allowing the material to flow and form a conical pile. The height of the pile and radius of spread (at base) were measured. The angle of repose was calculated from the triangle formed from these measurements (Ogunsina et al., 2009).

Coefficient of static friction μ on Structural surfaces

Three structural surfaces, ply wood, mild steel and aluminum, were used on incline plane. The plane was gently raised and the angle of inclination at which the sample started sliding was recorded. The tangent of that angle was taken as the coefficient of static friction μ.

Determination of Chemical Properties:

Micronutrient contents (calcium, potassium, sodium, and phosphorus) of the ground shells were determined in accordance with the methods of AOAC,(2006).

RESULTS AND DISCUSSION

In Table 1, it is observed that the equivalent diameters D_e for each type of mullusc shell differ according to the size range, except that of the periwinkle which had almost the same size. Sphericity (ϕ) and aspect ratio are almost the same irrespective of size range for clam shells, periwinkle and water snail shells. It is highest for water snail shell,

Table 1. Size Parameters and crushing strengths of selected mullusc shells for different size groups (10 replicates)

Type of shell	Size range in (percentile -%)	Equivalent diameter D_e(mm),	Sphericity, ϕ, $\frac{(D_e)}{L}$	Aspect ratio W/L	Crushing load (kN)	Surface Area of shell, cm^2	Crushing strength N/mm^2 (MPa)
	90	91.23	0.611	05.535	85.0	2.40	0.282
Land snail		86.15	0.589	0.462	79.25	3.86	0.489
	50	71.43	0.529	0.444	48.12	2.06	0.429
		64.20	0.510	0.429	45.0	3.39	0.753
		60.12	0.495	0.431	40.0	2.05	0.513
	90	57.62	0.876	0.838	31	0.77	0.248
Water snail		56.62	0.853	0.838	30	0.47	0.156
	50	37.77	0.837	0.816	23	0.69	0.300
		28.94	0.847	0.827	22	0.78	0.355
	85	57.92	0.780	1.35	65	32.76	5.04
Clam		55.36	0.770	1.34	55	11.63	2.115
	50	49.96	0.740	1.23	45	7.84	1.742
		42.20	0.715	1.29	44	15.11	3.434
		42.69	0.726	1.28	42	15.53	3.70
	80	24.38	0.597	0.468	5.00	8.28	16.56
Periwinkle		22.86	0.592	0.468	5.00	8.25	16.50
		22.66	0.599	0.476	5.00	5.62	11.24
		21.99	0.559	0.439	6.00	10.89	18.12
		21.52	0.547	0.441	4.9	8.19	16.71

followed by clam shell. Aspect ratio is higher for the clam shells and the water snail shell comes next. The percentile indicated in the size range shows the percentage of population that comes under that size. There are still bigger sizes in the upper percentile but were not available for the work.

Table 1 also shows the crushing strengths of these Oyster shells. The water snail shell has the least crushing strength, followed by that of the land snail. The periwinkle shell has the highest crushing strength, followed by the clam shell. These two shells are often crushed for livestock feeds and soil liming. The periwinkle shell is very hard and because of its small size, it is often used as aggregate for concrete. The clam shells are very hard too and with even higher crushing load than the periwinkle. However, because of its larger size, its average crushing strength is lower than that of the periwinkle.

It may be observed that some shells of the same mullusc but of smaller sizes may require higher crushing loads than big ones. This may be due to age or some special features in it such as cracks (Fellows, 2000). Cracks are weak points in the shell and so will require less crushing load. The clam has a knob in the head which is very hard. The periwinkle shells have spines. They require high loads to break them.

Table 2 shows some physical and mechanical properties of the ground mullusc shells. True density value (e_t) for each ground shell is greater than that of the bulk density. This is because the voids containing air spaces are excluded during true density measurement. The porosity of the ground clam shell was the lowest and differed greatly from those of other shells which had almost the same value. The low porosity value is an indication of less voids in the ground sample when packed in a container (Ogunsina et al., 2009). This sample took a little more time than others during grinding of equal weight of samples.. It shows it is a hard shell. The angle of repose for all the samples were almost the same. The coefficients of static friction on structural surfaces show that mild steel had the highest values and aluminum surface the lowest. However, the differences are not much and the same hopper inclination and incline surfaces can handle all these ground materials. However, the inclination of the surface such a machine part should not be less than or greater than the average value of these angles of inclination by much difference.

Table 3 shows some of the major micronutrients determined in these shells. Calcium, in particular, is needed for livestock feeds and for soil liming. It is highest in clam shell as shown in Table 3. It is even higher than in calcium carbonate which was used as a reference material. Akpabio (2006) showed that Ca in clam was about 2 times as much as in calcium carbonate. The clam shell is also seen to contain the highest amounts of K and Na Therefore it is a

Table 2: Physical and Frictional Properties of some Ground Mullusc Shells (4 replicates each)

Type of shell	True density ρ_t (gcm^{-3})	Bulk density ρ_b (gcm^{-3})	Porosity (%)	Angle of Repose (degrees)	Coefficient of friction on mild steel surface	Coefficient of friction on aluminum surface	Coefficient of friction on plywood
Land snail	1.82	1.28	29.67	9.37	0.554	0.488	0.649
Clam	1.67	1.35	19.20	8.58	0.649	0.466	0.577
Periwinkle	1.90	1.33	30.0	8.93	0.510	0.488	0.510
Water snail	1.82	1.30	28.57	7.96	0.532	0.445	0.510

Table 3. Chemical Analysis – Some Micronutrients of the Ground Mullusc Shells, mg/100g

Types of shell	Micronutrients (mineral) constituents (mg/100g)			
	Ca	K	Na	P
Land snail	6 x 10^3	21.00	8.8	1.25
Clam	10 x10^3	40.00	15.2	2.50
Periwinkle	8.25 x10^3	5.50	5.3	2.55
Water snail	8 x10^3	4.50	11.6	1.25
Calcium carbonate (Control)	8.8 x10^3	8.20	9.6	1.84

very important shell for livestock feeds and acid soil neutralization.

Conclusion

The sphericity and aspect ratio were almost constant for all sizes of shells of a particular mullusc.

This shows the possibility of a machine accommodating all sizes of the shells of a particular mollusk. The crushing strength was lowest for water snail and highest for the periwinkle shell. The clam shell was the richest in micronutrients determined (calcium, sodium, potassium and phosphorus).

Affordable crushing machines for small scale farmers to crush the shells without burning are possible. Particle size analysis of ground shells can help to determine the fineness suitable for liming certain soils and for animal feeds.

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