Effect of the Physicochemical Properties of Starch Adhesives on the Mechanical Properties of Composites from Cellulosic Materials Doped with Rust

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Abstract: The study examined the potential use of starch obtained from cassava and yam sources for the production of stable industrial adhesives that can be utilized in the production of composites. Cassava and yam tubers used in the study were obtained from Mowe and Ile-Ife (both in southwestern Nigeria) and washed free of sand and impurities before sun-drying. Starch and protein were then extracted from the cassava and yam tubers. The results indicated that both cassava and yam starches were suitable for this purpose. However, the particle size of the starch granules was found to be an important factor in determining the physicochemical properties of the adhesive. Composites produced with cassava starch adhesive were found to be more resistant to moisture than those produced with yam starch. Additionally, cassava adhesive was able to utilize more lignocellulosic fibers while still maintaining stability, provided that its limit was not exceeded. Furthermore, the addition of 2% metal additive (Fe^{3+} ions) improved the properties of the composites through coordination. Cassava starch-based composites were found to exhibit higher crystallinity than those produced with yam starch. The adhesive produced from these starch samples was found to be competitive with formaldehyde-based resins, with the added advantage of being non-toxic and capable of neutralizing the protons of acids with their excessive hydroxyl groups. Overall, the use of these cellulosic materials in the production of composites presents an environmentally friendly solution to the problem of waste and pollution. The study findings suggest that the starting materials are inexpensive, widely available, and environmentally friendly, and that they can produce products of greater economic importance.

Keywords: Cassava, Yam, Starch, Composite, Cellulose

1. Introduction

The need to rid our environment of waste, mainly domestic and agricultural in order to prevent environmental pollution that may arise from indecent disposal of such waste, necessitated the development of ideas targeted towards a more decent method of disposal, based on the conversion of waste into useful and commercially viable products that can easily compete other products in the market. In our environment today, especially, our citadel of learning, cellulosic wastes are very common, they are usually from the huge amount of papers used in so many of the activities which include; information dissemination, examinations, packaging and source of energy, just to mention a few. Unfortunately, the improper ways of disposing these cellulosic materials has made them a major source of environmental pollution, mainly caused by burning. Therefore, there is need to clean up the environment by converting them to useful items.

Items of interest are composites made up of the fibres of these cellulosic materials and binders. Attempts made on this issue had a major setback due to the adverse effects of the kind of binders used, these binders were mainly formaldehyde based and they are known to be a major source of formaldehyde toxicity which is associated with their use

and gradual release of formaldehyde into the atmosphere. Getting rid of this toxicity would in a way reduce the potential sources of carcinogens. Of interest in this study, is the use of naturally occurring binders based on existing starch sources such as tubers, grains, legumes and other sources known to be non-toxic.

Most white and soft papers used in printing and examinations are now being recycled into tissue papers, disposable hand wipes, just to mention a few and this is based on their soft nature and the method used in their pulping process. Neglected and allowed to rot in the environment are the packaging cellulosic materials (carton), which are usually hard, colored and can't be easily converted into other products. This nature can be associated with their pulping methods as well; they are to be utilized as the source of cellulosic fibres in this study.

Figure 1. *Waste packaging cellulosic materials (carton).*

Starch is a major carbohydrate reserve in plants and one of the most versatile biopolymers that is known to have an inexhaustible supply. Major starch sources include roots, tubers, cereals, grains, fruits and legumes; examples of which are yam, cassava, corn, wheat, rice and potatoes. Starch exists naturally as granules in plant cells. The accumulation pattern of starch granules in plant tissues as well as its composition and other physicochemical vary depending on the botanical source [1]. It is made up of two polymers: amylose (20 – 30%) and amylopectin (75 – 80%). Starch is used in biopolymer industries due to its ease of modification, biocompatibility, ease of use, biodegradability, its intrinsic physicochemical properties as well as its nontoxicity. In its native form, starch has limited industrial applications, and is usually modified to create novel properties as well as improved functionality [2].

Starch has been put to several uses, one out of many is its modification into adhesives. Some of the uses of this adhesive derived from starch include; composite bonding of disposable products (towel and tissue laminating, sanitary napkins and hospital supplies), the production of bags, labels, cigarette and filters just to mention a few. It has its application across other industries such as the pharmaceuticals, textile, construction, automobile and aircraft, the application of starch adhesives can't be exhausted [3]. The present study was therefore designed to modify starch samples using chemical processes and metal additives in enhancing their adhesive properties.

2. Experimental

2.1. Sample Collection and Pre-Treatment

The cassava and yam tubers used for this study were obtained from a farm in Mowe town, Obafemi Owode Local Government Area, Ogun State, while, the yam tubers were got from the Central Market in Ile-Ife, Osun State. The freshness of the tubers and their availability were the major factors considered in the choice of tubers used in the study. The collected samples were washed free of sand and other forms of impurities, before sun-drying up their surface water. Some of these yam and cassava tubers were kept for proximate analysis after determining their weights using the CAMRY Standard Scale with model number TCS-150-ZE21.

2.2. Extraction of Starch

The cassava and yam tubers were thinly peeled into distilled water to prevent the loss of the fleshy and starch containing parts from being lost and they were re-washed to rid their surfaces of dirt and other impurities. Each of the peeled tubers was cut into smaller pieces and were soaked into separate bowls of water for about twenty-four hours, with continuous changing of the water to limit the possibility of fermentation. The soaked tubers were reduced to smaller particles using mortar and pestle, before blending with a Giant Korean Blending Machine with model number ST-601S. The properly blended tubers were further reduced into their finer forms using the milling machine that had been properly washed with detergents and a lot of water. The blended tuber samples were mixed with a lot of deionized water and stirred thoroughly before sieving into clean containers and the chaff were discarded. The sieved starch samples were allowed to settle overnight before the excess water was decanted [4].

2.3. Extraction of Protein from the Obtained Starch Samples

0.1 N sodium hydroxide solution was added in excess to the starch slurry and was properly mixed before allowing it to sediment. This resulted in the formation of a dark brown solution on the sedimented starch before it was decanted off. This process was repeated until the solution above the starch became colourless. The starch was then washed with distilled water, allowed to sediment before the water was drained off, sun-dried (Figures 2 and 3) and stored in transparent containers. This was done for the starch obtained from the two tuber samples used in this study.
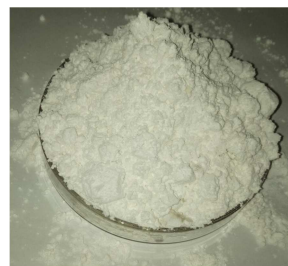

Figure 2. *Cassava Starch.*

***Figure 3.** Yam starch.*

2.4. Proximate Analysis of the Tuber Samples

The proximate analysis of the starch samples, using the fresh tubers was carried out at the Faculty of Agriculture, Department of Animal Science, Obafemi Awolowo University using the recommended methodologies of Association of Official Analytical Chemists [5]. The moisture content of each tuber samples were first determined, after which the tubers were subjected to drying in an oven at 38 ºC for twenty-four hours before other determinations such as the ash content, crude fibre content, Ether extract and crude protein of the tuber samples were carried out. These determinations were used to obtain the value of nitrogen free extract and total carbohydrate in the tuber samples.

2.5. Percentage Nitrogen Free Extract (%NFE)

Following the recommended procedure of the Association of Official Analytical Chemists [5], the Nitrogen Free Extract (NFE) was determined using the expression:

The Percentage Nitrogen Free Extract (%NFE):

%NFE = 100 – [Moisture + Ash + Crude Fibre + Ether Extract + Crude protein]

2.6. Percentage Total Carbohydrate

As previously provided by the Association of Official Analytical Chemists [5], the total carbohydrate of the raw sample was calculated using the equation:

% Total carbohydrate = % NFE + % Crude fibre

2.7. Physicochemical Tests for the Starch Extracts

The following series of tests were carried out on the extracted starch samples to ascertain their identities.

2.7.1. Identification Tests

1) *Iodine test*: About 1g of the cassava starch was boiled with 15 mL of distilled water and allowed to cool. A few drops of 0.1 N iodine were added to 1 mL of the mucilage in different test-tubes and the colour changes were recorded. The same procedure was repeated for the yam starch [6].
2) *Solubility test*: About 1g of each extracted from the two tubers was separately weighed and poured into glass beakers containing 1 ml of distilled water and stirred. This was repeated using 2 ml, 10 ml of distilled water and 95% ethanol solvents separately. The solubility of each starch samples were observed and recorded [6].

2.7.2. Acidity Test

About 10g of each starch extracts were added to separate beakers containing, 70% ethanol, the mixtures were shaken for about one hour, filtered. 50 ml of each filtrate was titrated against 0.1 N sodium hydroxide solution, using phenolphthalein as indicator, from which the volume of sodium hydroxide used is recorded, the procedure was done in triplicate and the mean value recorded as the acid value [6].

2.7.3. Determination of pH

About 5g of each starch extracts were weighed into separate beakers containing 15 mL of distilled water and was properly mixed. The resulting slurry was subjected to the pH determination using HI2209 digital pH meter. The suspension was poured into boiling distilled water to make up 100mL of the slurry. The slurry was allowed to cool before the pH measurements were taken again. The mixture was further cooked and allowed to cool and the final pH measurements were taken.

2.7.4. Physical Properties

Each starch sample was inspected for colour, odour, physical state and gelatinization temperature. The gelatinization temperature was determined by weighing 2g of each starch samples into 50mL of water and was heated to a temperature where 100% swelling of the solution was observed.

2.8. Determination of Other Properties of Starch Samples

2.8.1. Determination of Moisture Content of the Starch Samples

About 3g of each starch samples were weighed into petri dishes after which the combined weights of the petri dish and starch were taken. Each petri dish containing the starch sample was placed in an oven at the temperature of 110 ºC and left for 10 minutes to expel moisture [6]. This process was repeated until a constant weight was obtained. The moisture content was calculated using the equation:

$$\% \text{ moisture content of the starch} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:
W_1 = Weight of starch sample before heating
W_2 = Weight of starch sample after heating

2.8.2. Determination of Amylose/Amylopectin Ratio of the Starch Samples

About 2g of each starch samples were suspended in 50mL of distilled water in different beakers and a 1:9 mixture of butanol (5mL) and water (45mL) was added. The whole mixture was heated to boiling with continuous boiling. Another 1:1 mixture of butanol (5mL) and amyl alcohol (5mL) were added to the boiling suspension and allowed to cool in cold water bath. The supernatant liquor was decanted and the microcrystalline precipitate formed was repeatedly washed with butanol saturated with water, dried in an oven at 40º C and weighed. The procedure was

done in duplicate and the mean value was recorded as the ratio of the amylose for the two samples. The supernatant was precipitated with excess methanol and was filtered. The precipitate was dried in an oven at 40º C and weighed. The procedure was also carried out in duplicate and the mean value was recorded as the ratio of the amylopectin for the two samples [7].

2.8.3. Determination of the Flow Properties of the Starch Samples

The flow properties were measured using the angle of repose determination described: A funnel was mounted on a laboratory stand at 10cm from the bench. About 50g of each starch sample was poured into a funnel with the tip closed. The tip plug was removed and the starch was allowed to pass through the orifice to make a heap. The height and diameter of the starch heap were measured. The angle of repose, Ɵ, was calculated using the equation [6]:

$$\Theta = \tan^{-1}(h/r)$$

Where:
h = height of the starch heap and
r = radius of the circular base

2.8.4. Determination of Starch Density

This was determined using different parameters involving the following:

1) Bulk Density Determination

About 5g of each starch extracts were poured through a short-stemmed glass funnel into a 200ml graduated cylinder and the height occupied by the starch granules was read. The volumes and bulk densities for all starch extracts are then calculated using the equations [6]:

$$\text{Bulk Density} = \frac{\text{Mass of starch sample}}{\text{volume occupied by the starch}}$$

Volume = $\pi r^2 h_b$
Where h_b is the bulk height

2) Tapped Density Determination

Graduated cylinders containing each of the starch extracts from the bulk density tests were tapped on a bench 50 times and the respective heights were recorded and volumes were calculated [6]. The tapped density was calculated using equation:

$$\text{Tapped density} = \frac{\text{Mass of starch sample}}{\text{volume occupied by the starch}}$$

Volume = $\pi r^2 h_t$
Where h_t is the tapped height.

3) Carr's Index

This was obtained from the difference between the tapped and bulked densities divided by tapped density [6]. The ratio was expressed as a percentage in equation:

$$\text{Carr's index} = \frac{\text{Tapped Density} - \text{Bulk Density}}{\text{Tapped Density}}$$

4) Hausner Ratio

The ratio of tapped density to bulk density was calculated for the starches [6] using equation:

$$\text{Hausner Ratio} = \frac{\text{Tapped Density}}{\text{Bulk Density}}$$

5) Determination of the Swelling Power of the Starch Extracts

The tapped volume occupied by 10g of each starch extract were determined. The starch samples were then dispersed in 85mL of deionized water and the volume was made up to 100mL with more deionized water. They were then allowed to stand for eighteen hours before the volume of the sediments were then determined [6] and the swelling capacity was calculated from the difference in the volumes as shown in equation:

Swelling Capacity = Volume of Sediment – Tapped Volume

2.9. Production of Paper Particles and Adhesives

Waste cellulose-based paper materials (brown carton commonly used in packaging) were shredded into smaller sizes after removing the part that was printed on. The shredded cartons were soaked in water for twenty-four hours and 5mL of concentrated hydrochloric acid was added to prevent disintegration through bacteria infestation. The soaked cartons were pounded using a mortar and pestle, before being blended into fine particles. The blended carton was sieved and sun-dried. The dried carton particles were blended into powder using dry mill and were stored in transparent containers.

The two types of adhesives produced from the starch obtained from the tuber samples are:
i.   General office adhesive (gum)
ii. Industrial adhesive

2.9.1. Production of General Office Adhesive (Gum)

About 2.5g of each starch extract was poured into a beaker containing 50ml of 0.01M hydrochloric acid solution and heated to about 100 ºC with stirring. The resulting slurry was cooled in a cold-water bath and stabilized. The cooled slurry was heated to 70ºC after which 10% Borax (disodium tetraborate decahydrate $Na_2B_4O_7.10H_2O$) was also added while stirring the viscous mixture. 40% Sodium Hydroxide solution was added to the mixture to give maximum thickness. The mixture was stirred and then stored in a sealed transparent container and then stored [8].

2.9.2. Production of Industrial Adhesive

About 20g of each starch extract was poured into a beaker containing 15mL distilled water, stirred to give a suspension and 30mL of boiling distilled water was added. The resulting gel was further cooked for about five minutes before 2mL of 0.01M hydrochloric acid was added, giving a viscous mixture. About 0.40g Borax (2% by weight of the starting starch weight) was added to distilled water just enough to give a suspension. The borax suspension was added to the viscous mixture, homogenized by stirring, after which 6ml of 40% (w/v) sodium hydroxide solution was added to give maximum thickness to the viscous mixture [9].

2.10. Instrumental Analysis

2.10.1. Fourier Transform Infrared Analysis

A little part of each of the samples, adhesives, Particle-Starch adhesive composites of different mixing ratios and those infused with rust (Fe^{3+} ions), were cut and reduced to fine nanoparticles by pounding in mortar. 5g of each of the resulting nanoparticles were weighed into well-labelled sample bottles and were subjected to the Fourier Transformed Infra-red Analysis at the Central Science Laboratory, Obafemi Awolowo University using the Agilent CARY 630 Fourier Transformed Infra-red Spectrometer with serial number MYL9152002.

2.10.2. Elemental Analyses

About 5 g of the extracted starch samples were packaged and analysed for their elements particularly their metal contents using the Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrophotometer at the African University of Science and Technology, Abuja.

2.10.3. Mechanical Measurements

The composites produced were subjected to mechanical analyses at the Department of Material Science and Engineering, Obafemi Awolowo University. The series of tests carried out are presented below.

2.10.4. Microstructure Examination

Each composite was cut in the dimension (30×20) mm and were examined under the Accuscope metallurgical microscope with serial number 0524011. The pictures obtained were then studied and interpreted to determine the microstructures of the composite.

2.10.5. Hardness and Shearing

The composites used for the microstructure examination were subjected to Brinell hardness test and the punch-shear tests using Mosanto Testing Machine. The values obtained were recorded accordingly.

2.10.6. Compressive Strengths Measurement

Each composite was cut in the dimension ($12.7 \times 12.7 \times 24.5$) mm, before they were placed between the compressive plates of the Universal Instron Digital Machine with model number 3699 where they were compressed at a uniform rate. The values obtained on the monitor were recorded and automatically plotted and used to calculate the compressive strength of each composite.

2.10.7. Tensile Strength Measurement

The composites shaped to correspond to the standard cross-sectional area used in the Instron machine with the two terminal ends having a larger cross-sectional area than the middle part. The terminal ends were gripped by the Universal Instron machine with model number 3699, applying weight to the composite at one end and the other end is kept fixed, until it fractured. The forces responsible for each fracture were recorded and automatically plotted in a graph in order to calculate the tensile strength of each composites.

3. Results and Discussion

3.1. Availability of the Sample

The two tuber samples were readily available due to the ease of their cultivation and their role as a major source of dietary starch, carbohydrate and fibre.

3.2. Properties of Extracted Starch

3.2.1. Percentage Yield of Starch

The quantity of starch present in each tuber as presented in Table 1 showed that the cassava sample contained more starch than the yam with values of 14.1% and 9.2% respectively. This may be due to the moisture content in the samples because the higher the moisture content, the lower starch content [4].

Table 1. Percentage Yield of the Extracted Starch.

Sample	Weight of Sample (g)	Starch Yield (g)	Percentage Yield (%)
Cassava	3000	423	14.1
Yam	3000	276	9.2

3.2.2. Proximate Analyses

The proximate analyses carried out on the tuber samples indicated that the yam contained a higher amount of moisture as compared to the cassava (Table 2). This may be responsible for the higher yield observed in the cassava starch sample. It was also observed that the crude fibre, crude protein and the total carbohydrate followed the same trend.

Table 2. Proximate Analytical details of Tuber Samples.

Sample	Moisture (%)	Ash (%)	Crude Fibre (%)	Ether Extract (%)	Crude Protein (%)	Nitrogen Free Extract (%)	Total Carbohydrate (%)
Cassava	56.58	2.03	1.89	0.41	3.06	36.03	34.42
Yam	59.37	1.25	1.96	0.35	6.56	30.51	35.97

The convergence of the crude protein indicated the presence of nitrogenous compounds such as amino acids and lignin which is responsible for the brown-coloured solution that was observed when the starch was treated with 0.1 N sodium hydroxide. The fibres were suspected to be in form of collagen and keratin. This is expected to further enhance the

bond ability and the strength of the composites made from the sample [10]. Nitrogen free extract in the cassava starch was greater than that of the yam, also confirming that it contained a lower amount of protein as compared to the yam starch.

3.2.3. Identification Test

This was carried out to confirm whether the obtained products were starch. The iodine test carried out on the sample gave positive results with the emergence of blue-black colour. All the starch samples were insoluble in both water and ethanol irrespective of the concentration used, instead of getting a clear solution, a colloidal dispersion was

observed. This is one of the characteristics of starch.

3.2.4. Moisture Content

It was observed that the starch obtained from the two samples showed a relatively low moisture content but the cassava starch had a higher moisture content as compared to that of yam (Table 3). This is a reversal of the moisture content observed in their tubers (Table 2). This can be attributed to the texture and the particle size of the starch samples. It was observed that the cassava starch had finer and smaller particles than the yam starch. The smaller the particle size, the greater the surface area which results in an increase in moisture absorption [11].

***Table 3.** Moisture content of the Starch Samples.*

Tuber Sample	Weight of Starch (g)		Moisture Content
	Initial weight	Constant weight	
Cassava	3.00	2.30	0.70
Yam	3.00	2.50	0.50

The difference in the particle sizes of the extracted starch samples may be due to the presence of crude fibre (which may include the lignin). The yam, containing a higher amount of crude fibre (Table 2) that must have contributed to the coarser texture of its starch. The relatively low moisture content of the starches makes them easy to store at room temperature.

3.2.5. pH and Acidity of Starch

The two extracted starch samples were positive to acidity

test as a result of their colour change they displayed but the level of acidity can be assumed to be small based on the small volume of sodium hydroxide utilized (0.46 and 0.57 cm^3 for cassava and yam starch respectively) in experiencing the colour change (Table 4). The volume of NaOH utilized gave credence to the pH of the extracted starch samples which are alkaline so they were unable to take up hydroxyl groups as expected so they quickly reached the neutralization points.

***Table 4.** Acidity and pH parameters of the starch samples.*

Sample	pH Test		Acidity Test		
Source	*Cold water*	*Boiled water*	*Cooked Sample*	*Vol. of NaOH (cm^3)*	*Colour Change*
Cassava	8.11	8.08	7.60	0.46	Colourless to light pink (Positive)
Yam	9.94	9.64	9.40	0.57	Colourless to light pink (Positive)

This will enhance the stability of the adhesive product produced by them because of its preference for a slightly basic pH for enhanced stability, bearing in mind that in an acidic medium, protons could rupture the polymer chain, or catalyze or initiate reactions between other additives of the adhesive, thereby leading to the degradation of the adhesive. Generally, the pH value reduces with an increase in temperature because an increase in temperature may also lead to an increase in the number of H^+ ions in the solution due to the dissociation of molecules and this is particularly true for weak acids and bases. Since pH is a measure of the hydrogen ion concentration, a change in the temperature of a solution will therefore be reflected by a subsequent change in pH [12]. This indicates that desired pH values of the adhesives can be

obtained by modifying the temperatures of the starches. An increase in any solution's temperature, will cause a decrease in its viscosity and an increase in the mobility of its ions in the solution.

3.2.6. Starch Swelling Power

The ability of the starch granules to absorb moisture that results in the increase in weight and size as represented in Table 5. This is related to the particle size of the starch granules. As previously reported that the cassava starch gave the higher moisture content due to its smaller particle size, the swelling capability of the extracted starch indicated that the cassava starch had a higher value than that of the yam due to its lower tapped volume that confirms the lower particle size.

***Table 5.** Swelling Capability of the Extracted Starch.*

Sample	Tapped Volume (cm^3)	Swelling Volume (cm^3)	Swelling Capacity (cm^3)
Cassava	38.75	44.27	5.52
Yam	40.27	43. 75	3.48

It can be said that the lower the tapped volume, the lower the starch particle size and the higher the swelling capacity.

Since the swelling capacity reflects the increase in volume of starch following water absorption, it can be assumed that the

yam starch would be more appropriate for use in the production of adhesives to be used in high moisture area. They can both be modified to produce perfect adhesives with little or no limitations. Starches swell in cold water and are partially dispersed in hot water, which is responsible to their thickness when cooked and samples with high swelling power cooks fast.

3.2.7. Starch Flow Properties

The values for the angle of repose used in determining the flow properties of the starch as presented in Table 6 showed that the yam starch had a lower value than the that of cassava.

Table 6. *Flow Properties of the extracted Starch.*

Sample	Height (cm)	Radius (cm)	Angle of Repose (Θ^o)
Cassava	6.25	4.70	0.93
Yam	6.00	4.70	0.91

The larger the particle size of the starch, the lower the flow. The yam starch exhibited a lower angle of repose because of its larger particle size. The flow properties of a powder is essential in determining its suitability as direct compression. The lower the angle of repose, the higher the flow properties of the starch. The smaller the particles, the higher the surface area and the greater the surface energy to attract the particles to each other leading to a better adherence of the particles and have a higher resistance to flow [4]. This can be assumed to be responsible for the more plastic composite observed with the use of the industrial adhesive made from cassava starch.

3.2.8. Starch Density

The results of the series of density measurements carried out on the starch samples are presented in Table 7. The bulk density of the cassava starch was greater than that of the yam, signifying a better compaction in the former than the latter. This bulk density increases with depth. This is in line with the observed tapped density which showed 0.56 gcm^{-3} for the cassava and 0.61 gcm^{-3} for the yam. Both results further confirmed the fact that the cassava starch will be denser than that of the yam due to the higher compaction experienced by the former due to its smaller particle size and tapped volume.

Table 7. *Density of the extracted starch.*

Sample	Density (gcm^{-3})		Carr's Index	Hausner's Ratio
	Bulk	Tapped		
Cassava	0.55	0.56	0.25	1.11
Yam	0.42	0.61	0.10	1.33

The Carr's index and Hausner's ratio values (Table 7) were all lower than 23%. This suggests that the two extracted starch samples would exhibit a good flow and compressibility [6].

3.2.9. Amylose/Amylopectin Ratio

Since starch is known to contain the amylose and amylopectin in different quantities, it was observed that the yam starch contained a higher amount of linear chain than the cassava starch due to the higher value of amylose obtained for the yam starch. Expectedly, the cassava starch showed a higher content of the branched chain as denoted by the higher quantity of amylopectin determined in it with values of 83.2% and 77.2% for the starch extracted from cassava and yam respectively (Table 8).

Table 8. *Amylose/Amylopectin Ratio of the Starch Samples.*

Sample	Amylose (%)	Amylopectin (%)	Amylose/Amylopectin Ratio
Cassava	16.8	83.2	0.21
Yam	22.8	77.2	0.30

The values obtained for both the amylose and amylopectin fell within the specified limit of 15 to 25% for the amylose and 75 to 85% for the amylopectin [6]. Amylose rich adhesives are usually stiffer, more resistant to fracture and less stretchable. Starch samples with high amylose-amylopectin ratios will show high adhering properties such as strength and bond formation than those with high amylose content [13, 14].

3.2.10. Electron Dispersive-X Ray Fluorescence (ED-XRF) Results

The results for the quantification of the elemental content in the starch extracts are given in Tables 9 and 10. Detected species and their concentrations can be assumed to depend on the location and the composition of the soil on which the tubers were harvested. Anthropogenic contributions may also affect the metal contents of the samples. The elements, especially the metals, apart from existing in their ionic forms, they may exist as salts or in the organometallic forms where they combine with the organics and appear more stable.

The addition of a metal-containing chemical additives further increased the concentrations of metals in the starch adhesive product. Hence, more cations are available for coordination and bond formation. Due to their ability to use the d-orbital characteristics in chelation, they are expected to enhance coordination and hence, crosslinking in the cellulose-adhesive composites. Metals play a major role in bond formation in the boards which usually results in higher and better mechanical properties [15].

Table 9. *ED-XRF Elemental content of the Yam starch.*

Elements	Conc Value	Conc Error	Unit
Ca	0.8946	±0.3434	wt.%
Mn	1.2804	±0.1678	wt.%
Zn	6.0910	±0.3379	wt.%
Fe	5.8747	±0.3295	wt.%
Ru	9.3892	±2.0816	wt.%
Cu	8.8684	±0.3953	wt.%
Mo	8.7344	±1.0923	wt.%
Ni	8.2924	±0.3825	wt.%
Br	1.2457	±0.1710	wt.%
Sr	2.7068	±0.3261	wt.%
Cr	1.1475	±0.1781	wt.%
Se	1.9478	±0.2048	wt.%
Co	4.0029	±0.2588	wt.%

***Table 10.** ED-XRF Elemental content of the Cassava starch.*

Elements	Conc Value	Conc Error	Unit
K	0.0000	±0.0000	
Ca	0.8292	±0.3334	wt.%
Mn	0.8743	±0.1382	wt.%
Zn	7.8378	±0.3799	wt.%
Fe	6.7427	±0.3507	wt.%
Ru	11.6153	±2.3484	wt.%
Cu	8.4002	±0.3792	wt.%
Mo	7.0535	±0.9896	wt.%
Ni	8.7181	±0.3890	wt.%
Br	2.1819	±0.2275	wt.%
Sr	3.3044	±0.3663	wt.%
Cr	1.1233	±0.1753	wt.%
Se	2.1444	±0.2153	wt.%
Co	3.1810	±0.2277	wt.%

3.3. Adhesive

Diluted hydrochloric acid (0.01M) that was added to the starch paste improved the gel consistency and reduced the paste viscosity due to depolymerization of the starch. The acid destroyed the hydrogen bonds between the starch molecules thereby reducing the starch granule size. The addition of the acid also decreased the amount of amylopectin by depolymerizing it, forming more of amylose chains with more free hydroxyl groups which favoured gel formation and increases the strength [16, 17].

The borax added was converted into a more active species (metaborate) by sodium hydroxide and it is represented below:

$$Na_2B_4O_{7+}7H_2O + 2NaOH \rightarrow 4Na[B(OH)]_4$$

The metaborate was able to form a complex with two starch molecules together, thereby increasing and stabilizing the gel viscosity, give the gel better fluids properties and quicker tack [18].

Addition of sodium hydroxide to the complex, lead to the dissociation of the complex, which resulted in the viscosity reduction of the complex. As the amount of sodium hydroxide added increases, the viscosity decreased [19]. Sodium hydroxide is also used to neutralize the acid added in the modifying stage, ensuring a neutral or slightly basic medium, bearing in mind that in an acidic medium, protons could rupture the polymer chain, or catalyze or initiate reactions between other additives of the adhesive, thereby leading to the degradation of the adhesive.

3.4. Mechanical Properties

3.4.1. Hardness

The values obtained from the Brinell hardness test of each cellulose-starch adhesive composites are shown in Table 11:

***Table 11.** Brinell hardness of the composites.*

Composite Formulation	Additive	HARDNESS (BHN)	
		Cassava	Yam
1:1		22.0	16.3
2:1		23.3	16.0
2:1	Rust (Fe^{3+} ions)	24.3	20.0
3:1		35.3	13.8

It was observed that the Brinell hardness of the composites using the cassava and yam adhesives indicated that the cassava-based ones were able to withstand higher forces when compared with the ones produced from the yam adhesives even with the variations in their mixing ratios. There was a deviation from this pattern in the 3:1 sample using the yam starch adhesive because it showed a lower value of hardness. This may be attributed to the nature if the starch used in the production which had a larger size, leading to a higher porosity and tapped volume as compared to the cassava adhesive such that the cellulosic fibre particles mixed with them encountered the space which led to the fracture. The higher strength recorded for the cassava based composites can be said to be due to the smaller inter-particle spaces within the matrices, resulting in a better cohesion between the adhesive and the cellulosic particles [20]. The general increase observes as the concentration of the cellulose particles increase could be due to the interaction between the -OH groups of these fibres and the nucleophilic sites in the adhesives that were generated by the modification of some of the -OH groups in their transformation into the adhesive that resulted in hydrogen bond formation.

3.4.2. Shear Strength

The obtained values for the shearing strength of the composites as presented in Table 12 below showed a decrease in strength as the concentration of the cellulosic fibre particles increases. This is the reverse of what was obtained with the hardness test.

***Table 12.** Shearing Strength of the composites.*

Composite Formulation	Additive	SHEAR STRENGTH (N)	
		Cassava	Yam
1:1		35.5	33.2
2:1		35.0	35.3
2:1	Rust (Fe^{3+} ions)	43.3	44.8
3:1		14.4	14.9

The sharp increase in the shearing strength observed in the composites doped with the Fe^{3+} ions in form of rust could be as a result of the additional bonds formed by the d-orbitals of the Fe^{3+} ions which further stabilized the composite thus requiring a higher energy bring them apart. The relatively low values observed in the 3:1 composite is said to be due to the uneven distribution of the binder which resulted in its inability to properly hold the particles which are in excess in place. It can also be said that the slightly higher strength observed in the yam adhesive composite as compared to that of the cassava can be attributed to the higher amount of water embedded in the yam starch resulting in a higher moisture content thus enhancing the formation of associative forces of which the hydrogen bond is the most prominent [21].

3.4.3. Compressive Strength of Composites

The composites from the cassava adhesive had lower compressive strengths when compared with those from the yam adhesive except for the (1:1) whose compressive strength was the lowest (Table 13). It was observed that the cassava adhesive composite (1:1) appeared to be more plastic

than its yam adhesive counterpart therefore the former was able to withstand a higher force by spreading them out to

prevent early rupturing unlike the yam adhesive composite (1:1).

***Table 13.** Comparative Compressive Strength of Composites.*

Composite Formulation	Maximum Compressive Strength (N/mm^2)	
	Cassava Adhesive Composite	Yam Adhesive Composite
1:1	706.87635	190.33100
2:1	426.02709	3441.17768
2:1 with Rust (Fe^{3+} ions)	701.03207	7009.13593
3:1	3553.30110	3646.37077

The higher compressive strength in the yam adhesive based composite can be attributed to their lower hardness which indicated that they will be able to withstand more forces or load without rupturing. The particle side of the yam starch containing more voids into which the cellulosic particles can move into on the application of force may be responsible for these observations. The exceptionally high value of 7009 N/mm^2 obtained for the yam adhesive based composite (2:1) embedded with rust may be due to the previously mentioned reasons coupled with the addition strength provided by the chelate forming Fe^{3+} ions that enhanced the semi-crystallinity of the composite resulting in an enhanced resistance to applied force. The low value obtained for the cassava adhesive based composite (2:1) that was embedded with rust may be due to its more crystalline nature which made it more brittle and unable to withstand the applied force than the yam adhesive based composite [22].

3.4.4. Tensile Strength of Composites

The comparative ultimate tensile strength as presented in Table 14 showed that the cassava starch adhesive (3:1) had the highest tensile strength while its yam starch counterpart had the least. This was similar to the trend observed in the hardness of these composites where particle size and compatibility of the starch were responsible for the property. In addition to this, the increase in the concentration of the cellulosic particles that was able to mop up the excess amount of adhesive by allowing the cellulosic fibres fill the pores present in the matrix and utilizing the -OH groups in forming hydrogen bonds that resulted in a strong composite [23]. The morphology of the adhesive also made the fibres shorter than those of the yam starch adhesive (Figures 4 and 5) therefore adhering to the binder maximally as compared to the yam starch composite of the same mixing ratio.
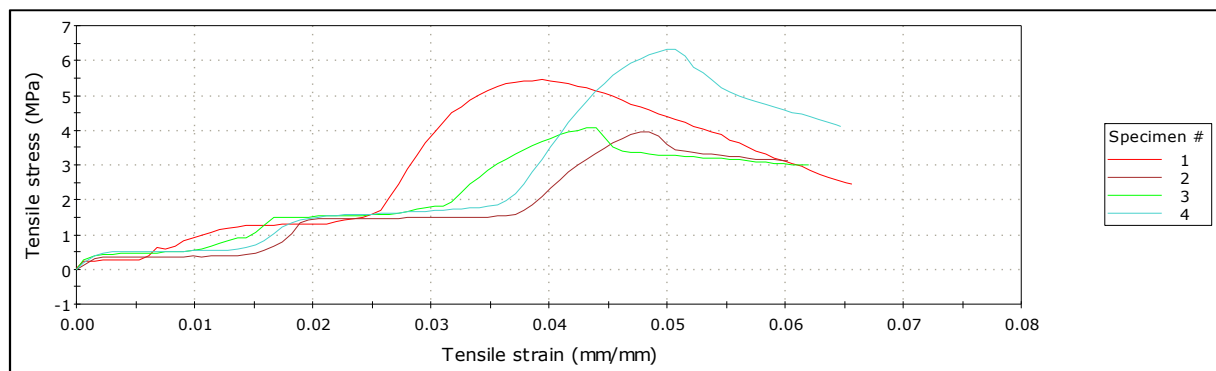

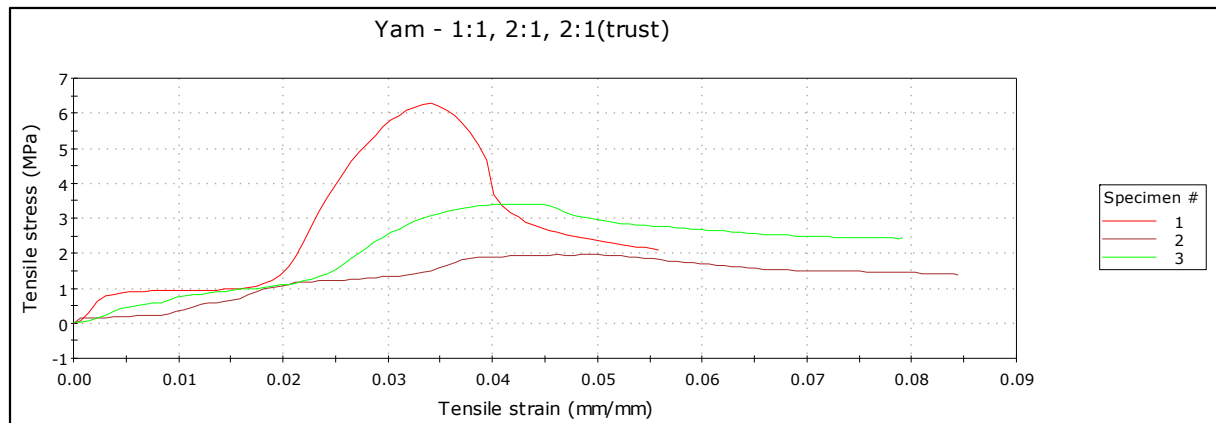***Figure 4.** Tensile properties of composites from cassava.*

***Figure 5.** Tensile properties of composites from yam.*

Table 14. Comparative Tensile Strength of Composites.

Composite Formulation	Ultimate Tensile Strength (N)	
	Cassava Adhesive Composite	Yam Adhesive Composite
1:1	359.36476	415.32218
2:1	261.48863	129.00959
2:1 with Rust (Fe^{3+} ions)	268.85681	225.28686
3:1	416.82585	42.15701

The lower value obtained for Cassava Adhesive Composite (1:1) as compared to the Yam Adhesive Composite of the same mixing ratio, was attributed to the presence of a lot of pores in its matrix despite having relatively short fibres covered by the adhesives making it more plastic than the Yam Adhesive Composite whose fibres appeared even shorter with fewer pores.

The stabilizing effect of the presence of the Fe^{3+} ions was observed in both the cassava and yam adhesive based composite (2:1) doped with rust was observed with the improved tensile strength observed in the composites of the same ratio, with the cassava adhesive composite exhibiting a higher tensile strength. The chelating and crosslinking capability of the transition metal ions using the vacant d-orbitals may be responsible for this [15].

3.4.5. Microstructures of the Composites

The microstructures comparing the surfaces of the composites under the same magnification showed that the cellulose-cassava starch composite contained a series of short fibres with pores and limited inter-granular space due to the smaller particle size. This resulted in the relatively high compressive strength due to the ability of the composite to spread the force on impact that made it accommodate a higher force as compared to the one produced with the yam starch adhesive with very short fibres, pores but with larger inter-granular space due to the larger particle size of the yam starch granules. Fibres in the cellulose-yam starch composite (2:1) were shorter than those of the cellulose-cassava starch composite (2:1) despite the same concentration of fibres and also had more pores even though they were not as much as those in their (1:1) counterparts. The cellulose-yam starch composite (2:1) was able to accommodate part of the fibres in these pores so they appear shorter, much more embedded in the adhesive [24]. This reflected in its compressive strength being greater than that of cassava in both the undoped and the Fe^{3+} ion doped composites where the compressive strength of the cellulose-yam starch composite (2:1) was almost ten times that of the cellulose-cassava starch composite (2:1). The inverse relationship between the compressive and tensile strengths was exhibited. It was observed that the Fe^{3+} ion doped composites exhibited higher crystallinity with the fibres appearing more distinct within some gelatinous matrix holding them together. The composites (3:1) showed a larger number of long cellulosic fibres in both cases that were very obvious. This may be due to the higher quantity of the cellulosic fibres particles involved. This might be responsible for the relatively low values obtained for the tensile strength and hardness for the

cellulose-yam starch composite (3:1) that might have resulted from the over-saturation of the hydroxyl groups from the cellulosic fibres. The repulsive forces generated by this weaken the cohesive forces which eventually imparted on properties like the hardness, compressive and tensile strengths. the cellulose-cassava starch composite (2:1) was better in terms of hardness and tensile strength due to the smaller size of the starch granules and better compatibility [25].

3.5. Infrared Analyses

Composites with the 2:1 formulation that were relatively more stable in terms of their properties were used in these analyses. The Infra-red analyses of the samples and the cellulosic composites as presented in Table 15 indicated that there were possibilities of bond formation through the carbonyl -C=O group due to the shift observed from 1644 cm^{-1} for the cellulosic fibre to 1635 cm^{-1} for the cellulose-cassava adhesive composite, 1639 cm^{-1} for the cellulose-yam adhesive composite and 1636 cm^{-1} for the cellulose-yam adhesive composite doped with Fe^{3+} ions (rust). The observed reduction in absorption bands is an indication of bond formation through carbonyl functional group. An outright disappearance of similar band in the cellulose-cassava adhesive composite doped with Fe^{3+} ions (rust), was an indication of bond formation due to the distortion of the initial -C=O bond.

Reduction in absorption bands was also observed in the C-O-C group where the cellulose fibre gave an initial 1156 cm^{-1} and 1152 cm^{-1} for the cellulose-cassava adhesive composite without the iron additive and the cellulose-yam adhesive composite doped with Fe^{3+} ions respectively. For the cellulose-yam adhesive composite doped with Fe^{3+} ions, the functional group disappeared, which also indicates bond formation. The same value of 1152 cm^{-1} was obtained for the cellulose-cassava adhesive composite. Appearance of the metal-oxygen (M-O) bonds in the fingerprint region for all the composites, as compared to that of the binder and the cellulosic fibres, suggested the existence of additional bonds formed through the metals present in the sample and the Fe^{3+} ion additives. Bands between 1018 cm^{-1} and 1077 cm^{-1} could be assigned to bonds related to γ-FeO(OH), 700 cm^{-1} to 770 cm^{-1} could also be assigned to bonds related to α-FeO(OH) and 600 cm^{-1} to 680 cm^{-1} assigned to bonds related to δ-FeO(OH) [26]. All these are associated with the Fe^{3+} ions present in the rust additives. The bands at 3200 cm^{-1} to 3500 cm^{-1} which may be associated with the -O-H or -N-H bonds could not be assigned because they were not well defined.

Table 15. *FTIR Absorption bands for Experimental Samples and Composites in (cm⁻¹).*

Cassava Starch	Yam Starch	Cellulose Fibre	Fibre-Cassava Adhesive (2:1)	Fibre-Yam adhesive (2:1)	Fibre-Cassava adhesive + Rust (2:1)	Fibre-Yam Adhesive + Rust (2:1)	Tentative Assignment
3269	3280.1	3298.7	3288	3321	3276.8	3407 3302	Stretching O-H or N-H
2930	2929.7 2374 2084 1871	2892.4	2907 2084	2885 2363 2166 2133	2930	2896 2318 2099 1999 1938	Stretching C-H of alkanes
1640 1457 1334	1640 1409 1338	1644 1420	1635 1420 1364	1639 1424 1364	1416	1636 1420 1364	Stretching C=O of aldehydes Deformation C-H of methylene
1077	1148 1077	1156 1021	1152	1156		1152	Stretching C-O-C of ether Stretching C-O of alcohol
995 928	992 932		992	999	999	992	C-H bending of alkenes
708 615	761 705	656	753 667	663 603		753 716 678	M-O bonds

4. Conclusion

From this study it can be concluded that the starch obtained from the two starch sources were appropriate for the production of stable industrial adhesive that can be used in the production of composites. It was also established that the particle size of the starch granules is an important factor in the physicochemical properties of the starch. Composites produced with the cassava starch adhesive can withstand more moisture than those prepared from yam. Likewise, adhesive from cassava can utilize more lignocellulosic fibres and still remain stable, provided that its limit is not exceeded as compared to that of yam that easily exceeds the limit. Addition of 2% of metal additive (Fe^{3+} ions), improved the properties of the composites through coordination. The cassava starch based composites exhibit higher crystallinity than that of yam from the results obtained. Adhesives from the starch samples can compete with the formaldehyde based resins, with the advantage of their nontoxicity and their ability to neutralize the protons of the acids with their excessive hydroxyl groups. The use of these cellulosic materials in the production of composites will clean the environment and reduce pollution. This work should serve as a part of solution to the much discussed environmental waste problem. The starting materials are cheap, available and environmental friendly giving products that are of greater economic importance. Recycling of other waste materials into economically viable products should be further investigated.

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