UNIVERSITY OF LAGOS NIGERIA.

Evaluation of Mechanical and Thermal Properties of Polyester/Carbonized Maize Stalk Particulate Composites

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OUTLINE OF PRESENTATION

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INTRODUCTION

- Development of polymer composites using agro-wastes or lignocellulosic materials as reinforcements for eco-friendly composites is currently the focus of attention.
- Maize stalk ash (MSA) is one of such major agro-waste products and natural reinforcement, which contain cellulose, hemicellulose, lignin and ash.
- This natural reinforcement has been utilized in the manufacture of composite panels.
- Use of agricultural residues such as corn cob fibers, flax straw fibers, wheat fibers and bagasse as reinforcement in the production of plastic composites has alleviated the shortage of wood resources.
- These low cost lignocellulosic sources (agro-fibers) when combined with polymer matrices decrease overall manufacturing costs and increase stiffness of the composite materials.

ADVANTAGES OF AGRO-WASTES AS REINFORCEMENT IN POLYMER COMPOSITES

The use of agro-wastes as reinforcement in polymer have recently attracted the attention of researchers because of their advantages over other established materials. They are:

- environmentally friendly,
- fully biodegradable,
- abundantly available,
- cheap and
- low density.

WORLD PRODUCTION OF MAIZE /MAIZE STALK WASTES

Maize stalk
fresh

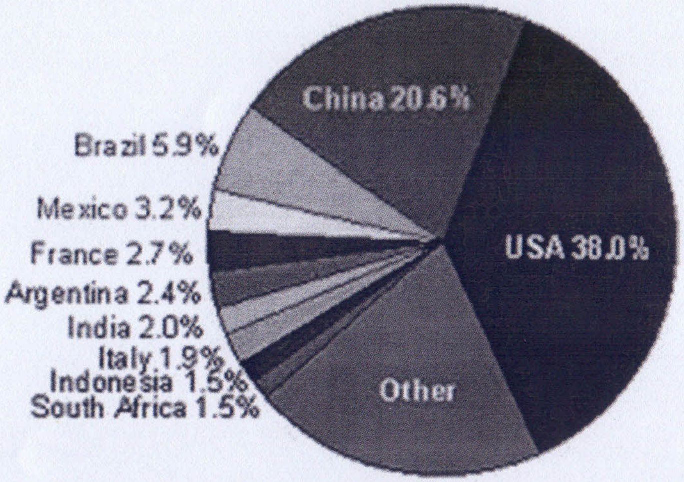

Figure 1: World Maize Production by Country. Other Countries produce 20% while USA , China, Brazil & Co. produce about 80%

Maize stalk wastes after harvest

Maize stalk wastes after harvest

Plate 1: Maize Production/Maize Stalk during harvest.

MAIZE STALK WASTES

- Maize (*Zea mays*) is of great economic importance. In developing countries such as Nigeria, the harvest of maize is very great.
- This increasing level of production is due to an increase of the cultivated areas which determines the total amounts of waste generated by the crop after the grain have been harvested.
- Maize stalk is commonly found in abundance and readily available in large quantity as waste after harvesting and other processing operations.
- Though, the waste is widely used for feeding livestock food, biological conversion to fuels but it is universally appears as waste material after industrial processing and other processes.
- They are non-toxic, environmentally friendly, fully biodegradable, abundantly available and are quite cheap.
- Frequently, the waste is usually burned as a means of waste disposal.
- In the light of petroleum shortages and pressure for decreasing the dependence on petroleum products, there is an increasing need in maximizing this waste material.
- Therefore, reinforcing polymer with maize stalk ash will have tremendous impact on the environment since polyester/maize stalk ash particulate composites will be partially biodegradable since the maize stalk ash is fully biodegradable.

PREVIOUS STUDIES ON MAIZE STALK

- Tavman (1996), discovered that the maize fibers have the potential of being used as reinforcing fillers in thermoplastics but they have a great disadvantage of moisture absorption and poor adhesion.
- Curtu and D. Motoc Luca (2009), successfully used maize fibers in polyethylene matrix composite but the primary drawback is the low processing temperature due to the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties.
- The mechanical properties of particle-polymer composite have been over the decades has attracted many researchers because of the improved properties it offers.
- Lombardo (2005), showed that the tensile strengths of nylon 6,6/kaolin/glass particulate composite increased when the interface adhesion is improved.
- Wang et al., (1998), found that the tensile modulus of hydroxyapatite (HA) filled polymer composites increased by 50–100% by adding 10%vol of kenaf particles.
- Similar results for other particulate–polymer composite systems have also been obtained.
- For example, Tjong & Xu (2001), observed that the tensile modulus of ternary polymer composites: polyamide 6,6 (PA6,6)/poly[styrene-b-(ethylene-co-butylene)-b-styrene] is enhanced by adding glass beats. Also, the modulus of epoxy/glass bead composites increases with glass beats.
- Similarly, Amdouni et al., (1992) found that the tensile modulus of nylon 6/silica nanocomposites increases constantly with increasing silica loading.
- Hence, addition of rigid particles to a polymer matrix can easily improve the tensile modulus of the polymer since the rigidity of the inorganic fillers is generally much higher than that of the organic polymers.

AIM OF THE STUDY

The aim of this study is therefore, to investigate the mechanical and thermal properties of carbonized maize stalk ash particles reinforced polyester composites in order to develop an engineering material for applications in automotive industries such as car bumper and in the building sectors such as house tiles.

MATERIALS AND METHODS

- The maize stalk used was obtained from a harvested agricultural farm.
- The base polyester resin, Cobalt Octoate (accelerator) and Methyl ethyl Ketone Peroxide (MEKP)(catalyst) were obtained from a Chemical shop.
- The collected maize stalk tegument was dried and ground to a fine powder.
- The fine maize stalk powder was carbonized at a temperature of 1200^0C in an electric resistance furnace in order to form the carbonised maize stalk ash(CMSA).
- The particle size analysis of the crabonised maize stalk ash was carried out in accordance with BS 1377:1990. A particle size of 53μm was selected and used.

SYNTHESIS OF THE COMPOSITES

- 5 - 25wt% carbonised maize stalk ash was used to produce the composites.
- In producing the reinforced polyester composites, the unsaturated polyester was measured into a 400 ml beaker and heated to 150oC and the carbonized maize stalk (CMSA) was added and then stirred vigorously until even dispersion was achieved.
- Addition of 1% weight of catalyst was made and stirred vigorously for another 3 min.
- 2% weight of accelerator was added to the mixtures and stirred vigorously for another 3 min before casting the sample into a mould.
- Initially, the mould was cleaned with acetone and coated with polyvinyl alcohol (PVA) and allowed to dry before the sample was cast. This procedure was repeated for all samples produced with changes in the percentage of the carbonized maize stalk particles.

MICROSTRUCTURES, MECHANICAL PROPERTIES AND THERMAL EXAMINATIONS OF THE POLYESTER/CMSAP PARTICULATE COMPOSITES

- The microstructures of the maize stalk ash particles, polyester resin matrix and the composites developed were carried out using SEM and EDS equipment.
- The mechanical properties (Tensile, Compressive, hardness and impact) were determined using standard techniques.
- Simultaneous thermogravimetric analysis (TGA)/ differential thermal analysis (DTA) was carried out in the Department of Chemical and Metallurgical Engineering, University of Johannesburg, South Africa.

RESULTS AND DISCUSSION

- The XRD result of the CMSAp is shown in Figure 2 while the chemical composition as obtained from XRD is shown in Table 1.

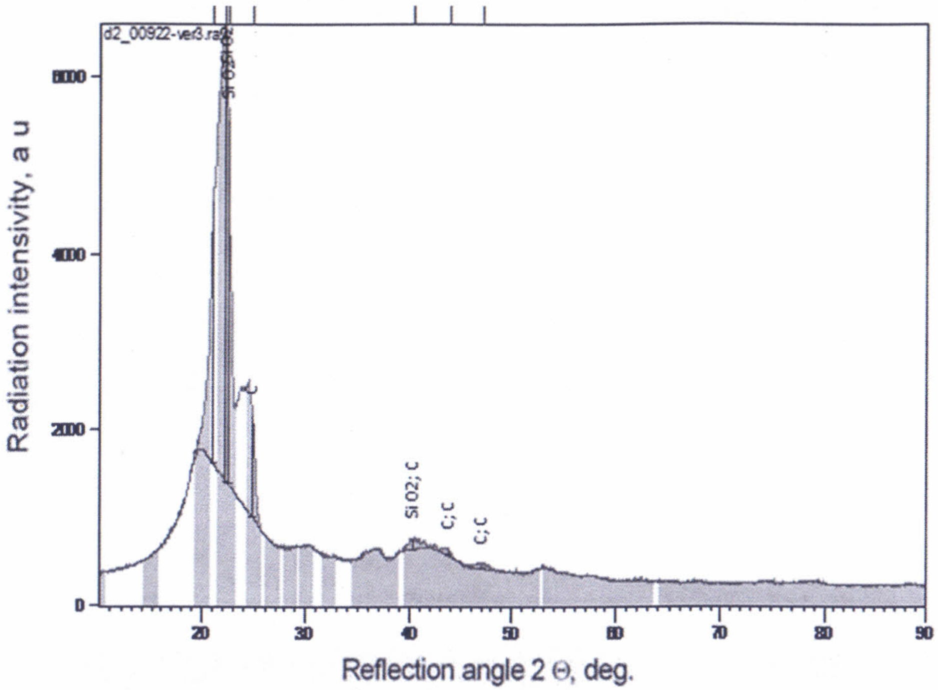

Figure 2: XRD pattern of CMSAp.

Table 1: Chemical composition of the CMSAp as obtained from XRD.

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-026-1081	31	Carbon	0.000	0.017	C
*	01-082-1555	28	Silicon Oxide	0.000	0.895	SiO_2
*	01-074-2329	25	Graphite nitrate	0.000	1.228	C

The XRD pattern obtained for CMSAp displays numerous diffraction peaks, which reflect the diffraction intensities of phases. The phases at these peaks are carbon (C), silicon oxide SiO_2 and graphite nitrate (C). The chemical/phase composition of CMSAp as obtained from the XRD are presented in Table 1.

- The XRD result of the polyester resin is shown in Figure 3 while the chemical composition as obtained from XRD is shown in Table 2.

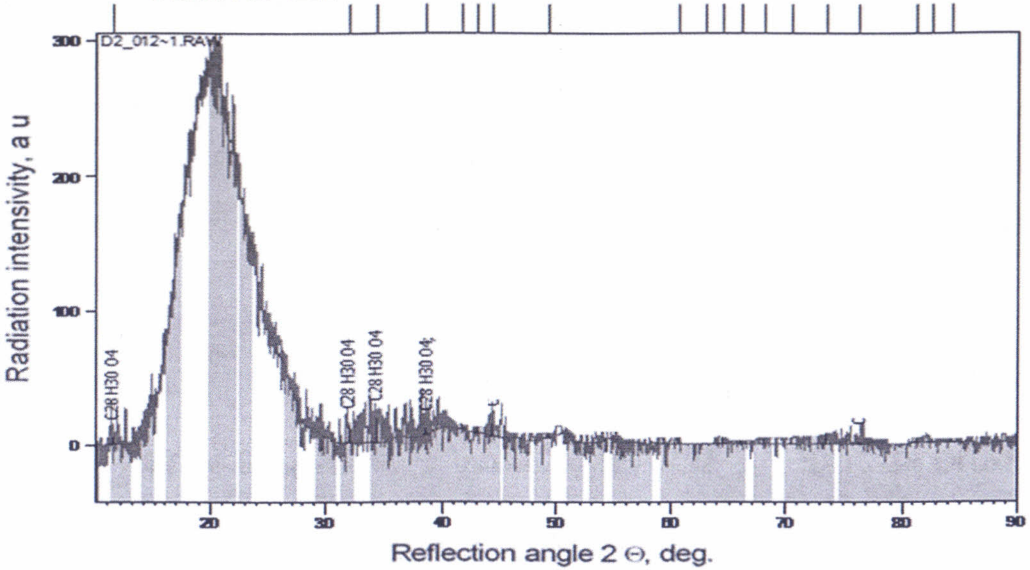

Figure 3: XRD pattern of the polyester resin.

The XRD pattern obtained for polyester resin displays numerous diffraction peaks, that reflect the diffraction intensities. The phases at these peaks reveal carbon (C) and 4,4'-Dihexanoyloxydiphenyldiacetylene as the constituents of the matrix. The chemical/phase composition of polyester resin as obtained from the XRD is presented in Table 2.

Table 2: Chemical composition of the polyester resin as obtained from XRD.

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-080-0017	27	Carbon	0.000	0.696	C
*	00-035-1959	48	4,4'-Dihexanoyloxydiphenyldiacetylene	0.000	0.313	$C_{28} H_{30} O_4$

- The SEM microstructure/EDS of the CMSAp and unreinforced polyester matrix are shown in Plates 3 and 4 respectively while that of the developed composites are shown in Plates 5 - 8.

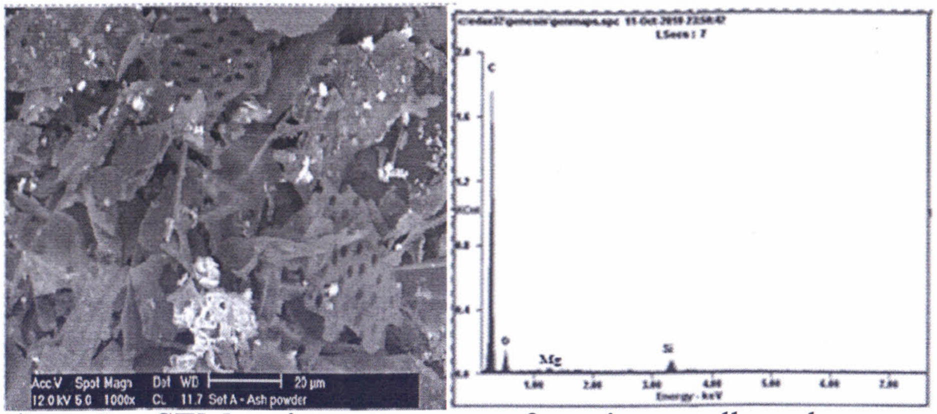

Plate 3: SEM microstructure of maize stalk ash particles (CMSAp)/EDS

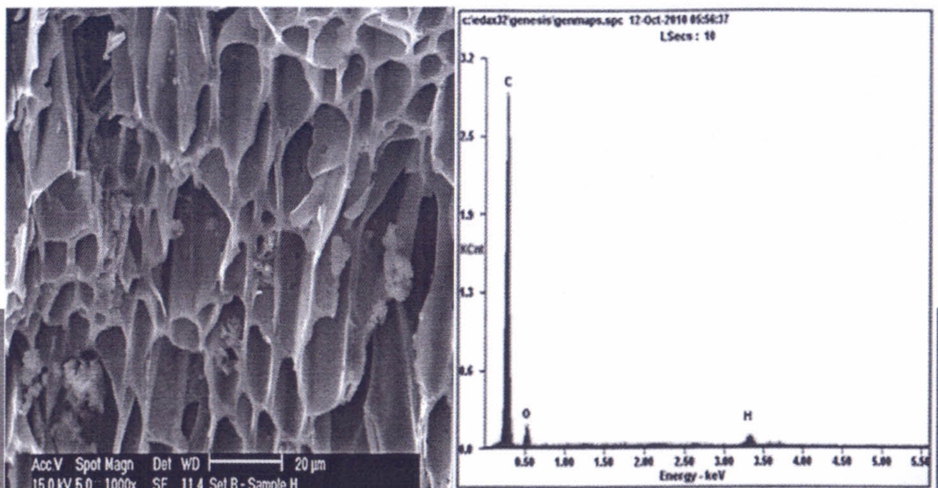

Plate 4: SEM microstructure of the polyester resin /EDS

- From the SEM microstructure of the carbonised maize stalk ash particulates (CMSAp) (Plate 3), it clearly reveals that the particle size and shape varies and they can be grouped into fibrous, prismatic and spherical.
- From the EDS spectrum it can be seen clearly that the elemental composition of the CMSAp was reveal.
- The polyester matrix (Plate 4) as revealed from the SEM spectrum shows the inter-lamina boundaries of the amorphous and spherulites structures. From the EDS spectrum it can be seen clearly that the elemental composition of the polyester resin was reveal.

- The SEM microstructure/EDS of the developed composites are shown in Plates 5 - 8.

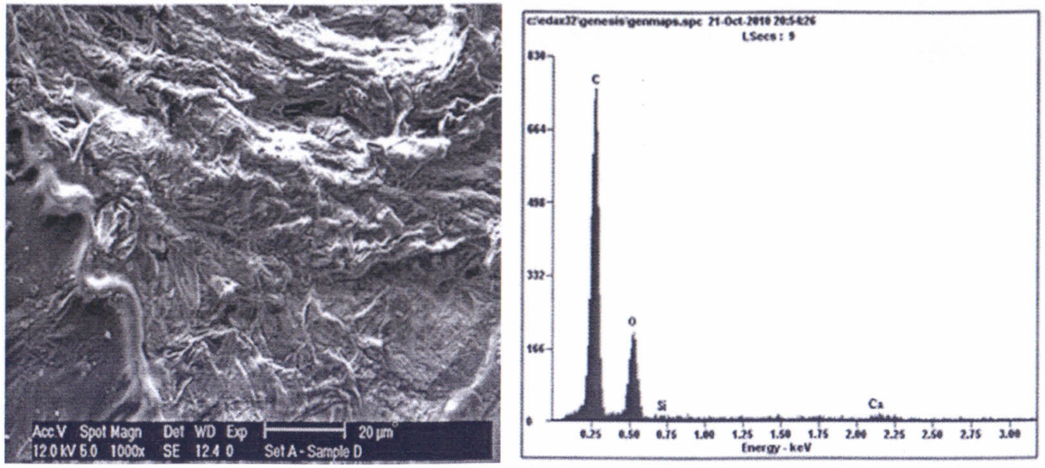

Plate 5: SEM microstructure of the 5wt% CMSAp reinforced polyester resin /EDS.

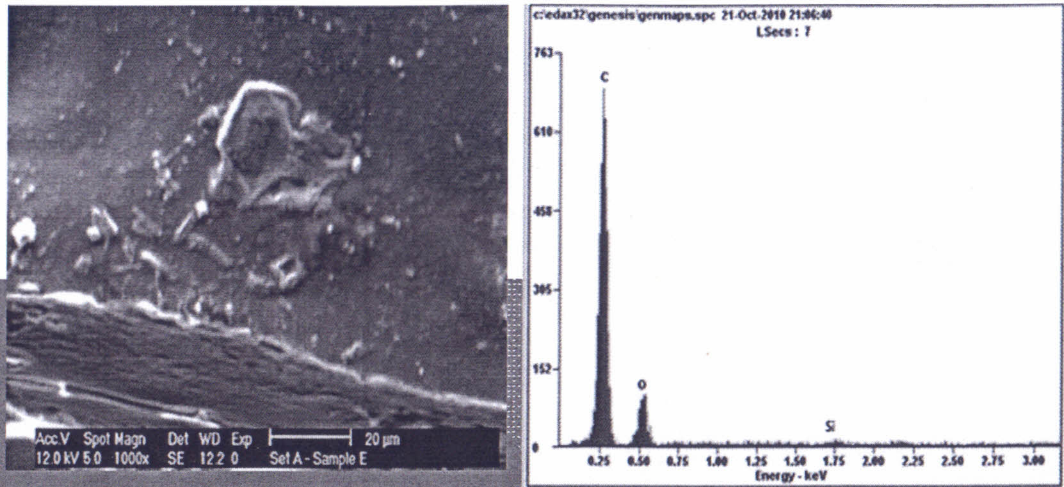

Plate 6: SEM microstructure of the 10wt% CMSAp reinforced polyester resin /EDS.

The SEM microstructural analysis shows clearly the difference in the morphology of the unreinforced polymer (Plate 4) as compared to those reinforced with maize stalk ash particulates (Plates 5-8). It can be seen that there is microstructural change as the maize stalk ash particles additions to the polyester increases.

Also, from the EDS spectrum it can be seen that the elemental composition of the composites developed were revealed. Plates 5-8 indicate a good and interfacial bonding between the CMSAp and the matrix.

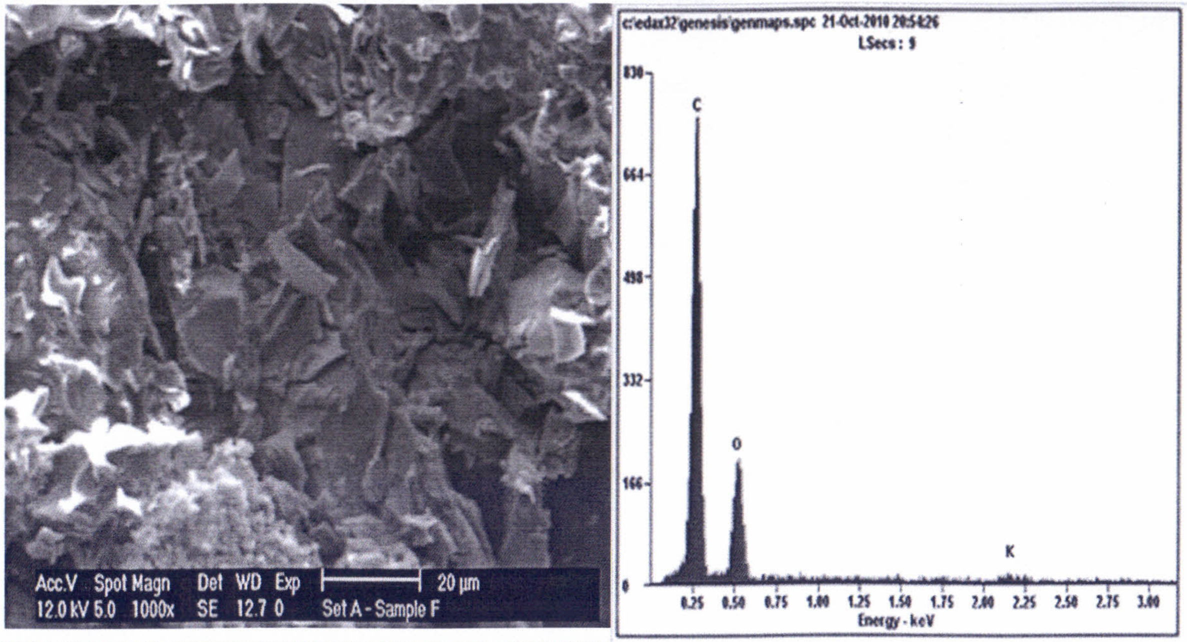

PLATE 7: SEM MICROSTRUCTURE OF THE 15WT% CMSAP REINFORCED POLYESTER RESIN /EDS.

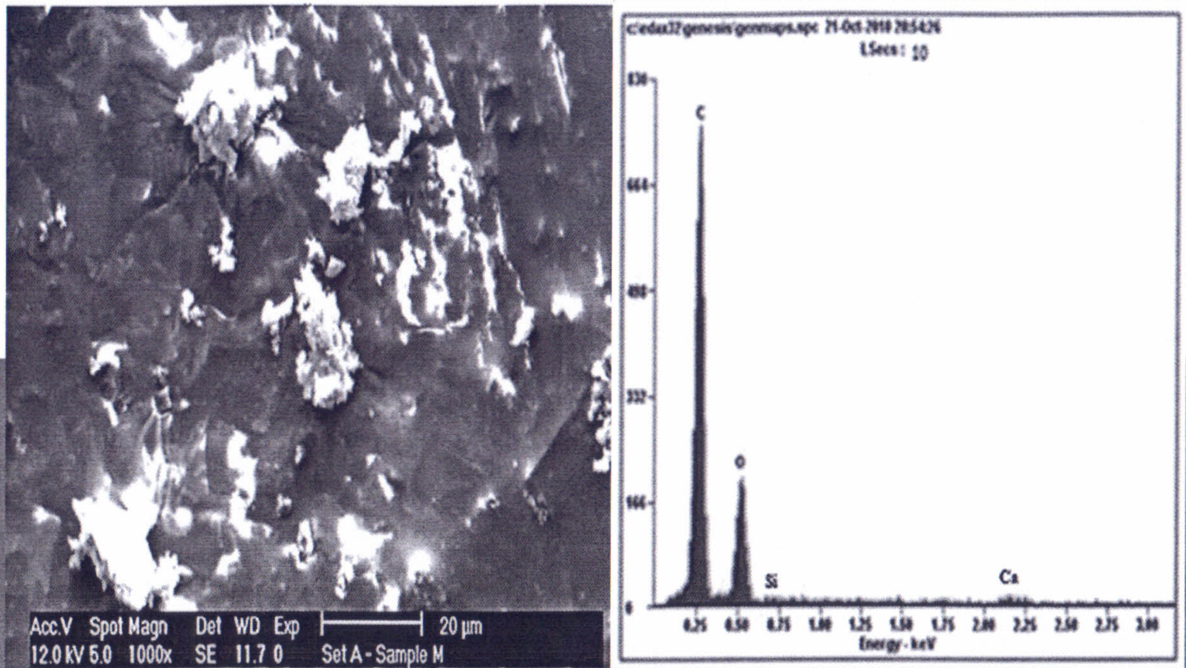

Plate 8: SEM microstructure of the 20wt% CMSAp reinforced polyester resin /EDS.

Table 3: Mechanical Properties of Carbonised Maize Stalk Ash particles reinforced Polyester Composites

% wt MSA Particulate	Tensile Modulus (N/mm2)	Tensile Strength (N/mm2)	Compressive Strength (N/mm2)	Impact Strength (J)	Hardness Values (HR)
0	159.55	35.10	19.12	0.90	19.70
5	203.65	39.52	20.20	0.88	26.10
10	421.74	48.50	25.50	0.87	36.30
15	794.56	50.46	29.78	0.85	48.80
20	824.62	53.60	30.32	0.78	57.80

Figures 4 - 7 show the variation of the mechanical properties with weight percent of CMSAp additions.

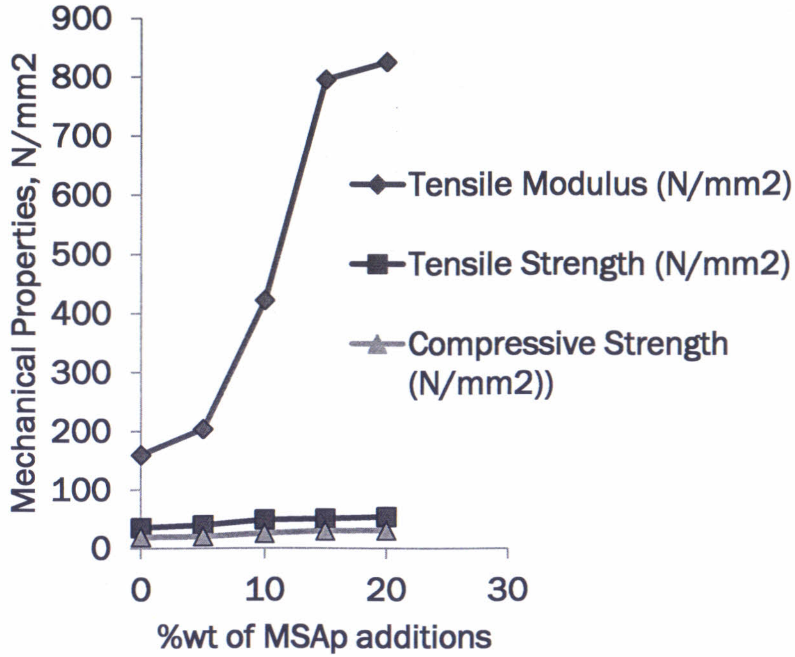

FIGURE 4: TENSILE AND COMPRESSIVE STRENGTHS OF POLYESTER/CMSAP COMPOSITE WITH CMSAP ADDITIONS.

The mechanical properties of particulate–polymer composites depend strongly on the particle size, particle–matrix interface adhesion, stress-strain behaviour of the filler and/or the matrix, and volume of particle loading.

The tensile modulus and tensile strength increases with increasing weight percent of CMSAp additions. This increase may be attributed to the higher crosslink density and good distribution of CMSAp in the polyester matrix.

This uniformity of CMSAp distribution efficiently hindered the chains movement during deformation.

These results are in agreement with the SEM results obtained (Plates 5-8) and also in agreement with earlier researches [Munoz, 2008 & Amdouni et al., 1992]. The increase in tensile strength of the developed composites is primarily because the developed composites contained well-bonded CMSAp, good CMSAp dispersion and strong polyester/CMSAp interface adhesion for effective stress transfer. This observation is in agreement with earlier research [Ismail et al., 1997].

The increase in the compressive strength of the developed composites is due to good interfacial bonding between the matrix and the CMSAp and uniform distribution of the CMSAp in the matrix. This leads to hardening of the matrix by the CMSAp.

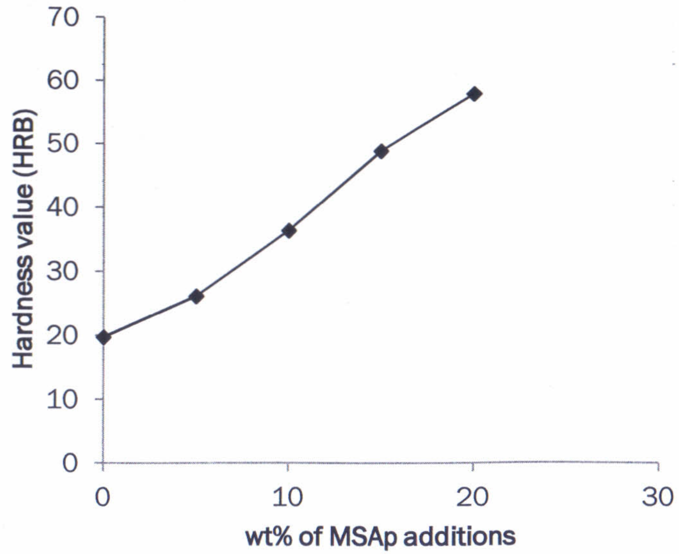

Figure 5: Hardness value with % wt of CMSAp additions.

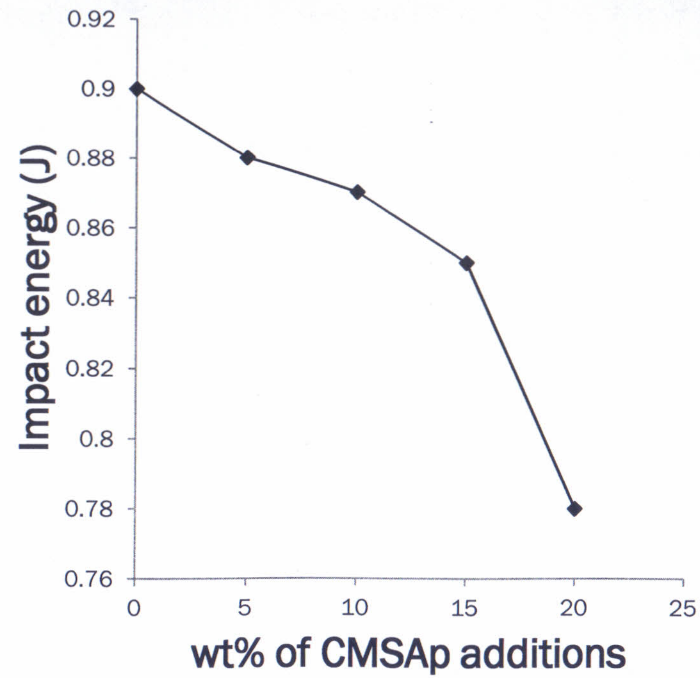

Figure 6: Impact Energy with % wt of CMSAp additions.

The hardness values of the developed composites increases with CMSAp additions (Figure 5). The increase in hardness is due to the increasing amount of hard and brittle CMSAp in the polyester matrix. These hard CMSAp continuously resisted deformation due to indentation.

The impact energy of the developed composites decreases with the addition of the MSAp (Fig. 6). This is because as the percent weight of MSAp additions increases, the energy absorption mechanism at the surface of the MSAp and the polyester/MSAp interface is not efficient. This means that the MSAp could not pin down the crack formed effectively thereby the velocity of crack propagation through the polyester matrix increases. This observation shows that all the dissipated energies during the impact test are only absorbed by the polyester matrix without positive contribution from the MSAp to enhance the impact energy. This is in agreement with earlier findings .

RESULTS OF THE TGA/DTA EXAMINATION OF THE POLYESTER/ CARBONIZED MAIZE STALK PARTICULATE COMPOSITES PRODUCED ARE SHOWN IN FIGURES 7 – 10.

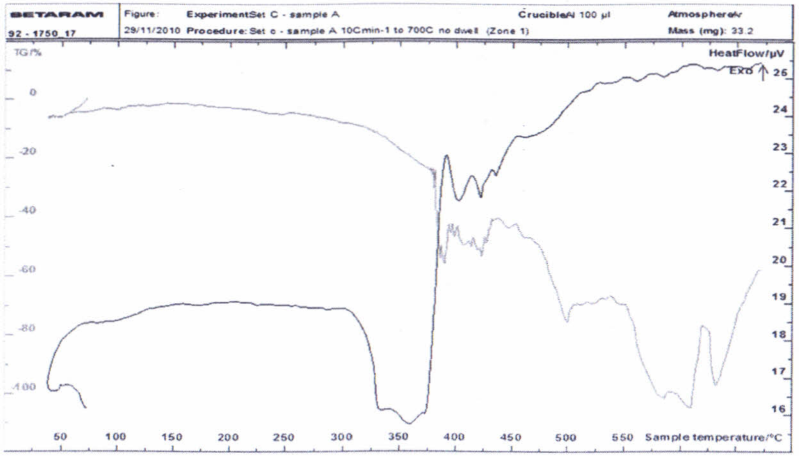

Figure 7: DTA/TGA Analyses of the polyester resin.

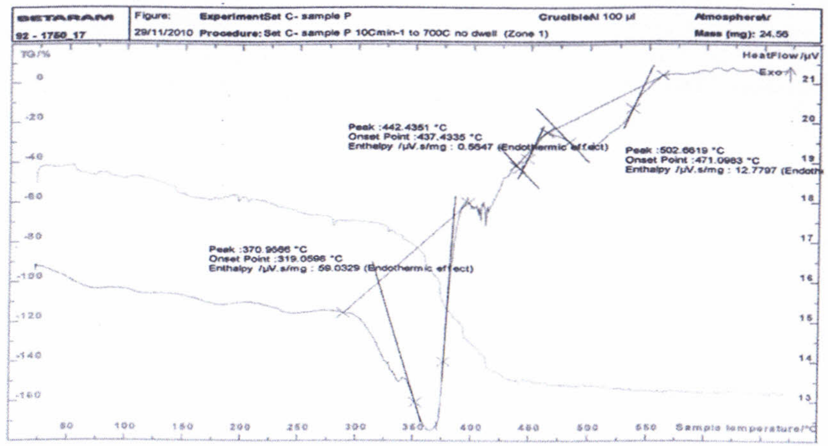

Figure 8: DTA/TGA Analysis of the polyester/5wt%CMSAp composite.

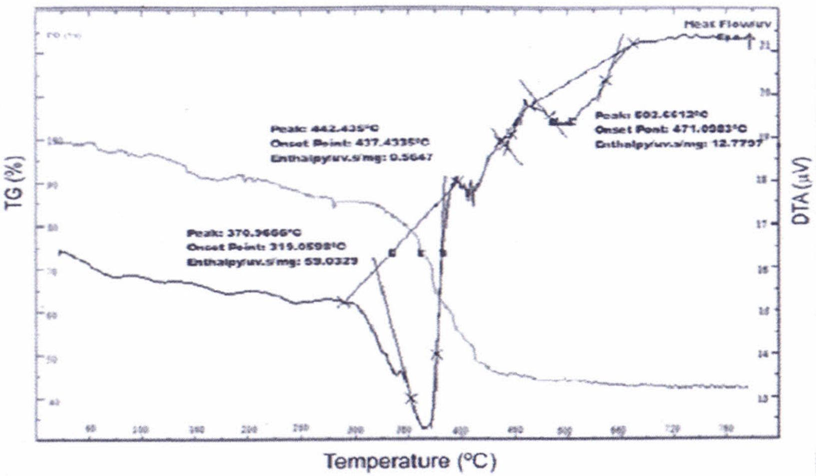

Figure 9: DTA/TGA analyses of the polyester/10wt% CMSAp composite.

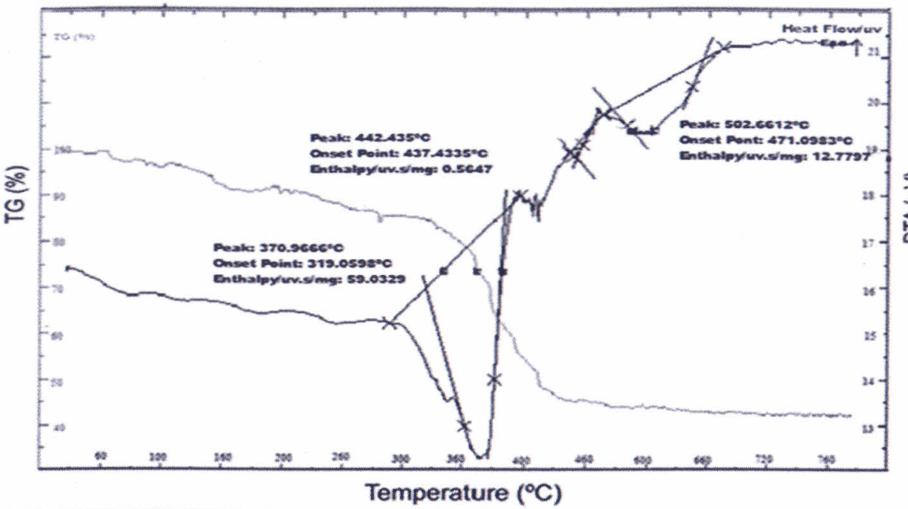

Figure 10: DTA/TGA analyses of the polyester/20wt% CMSAp composite.

THERMAL RESISTANCE OF THE DEVELOPED COMPOSITE

- In the polyester resin, the process of depolymerisation commences between the temperature ranges of 100°C-160°C followed by cleavages of C-H, C-C and C-O bonds (Figure 7) while the initial and final decomposition temperature (IDT) and (FDT) of this polymer occur at 300°C and 675°C respectively .
- On the other hand, the polyester/CMSAp composites generally have an initial decomposition temperature ranges of 320-328°C and final decomposition temperature of 800-818°C (Figures 8-10).
- The increase in the value of the initial and final decomposition temperatures is attributed to carbon, silica and graphite on the interface of the polyester/CMSAp composite which does not easily burn off in oxidative medium thereby delaying the thermal degradation of the polyester/CMSAp composite.
- However, analysis of polyester/CMSAp composite using DTA produces various peaks that are likely due to the fact that the composite contains a fraction of carbon and/or with functional groups (i.e., the material is oxidized at higher temperature).
- The positions of each of these peaks have been attributed to various components in the composite material (amorphous carbon, graphitic particles).

CONCLUSIONS

- From the mechanical and thermal analyses of the polyester/maize stalk ash particulate composite produced, it has been shown that maize stalk ash particles can be used as source of reinforcement in polymer matrix composite.
- The results obtained show that the developed composites have improved thermal stability as compared with the polyester resin.
- This research has added another agro-waste and biodegradable material to the several types used for reinforcement.
- It can be concluded from results obtained that the developed composites have shown improved mechanical and thermal properties as compared with the unreinforced polyester resin.
- That the developed composites has shown improved mechanical properties as compared with the unreinforced polyester resin except that there is slight decrease in the impact energy as the [illegible] waste maize stalk ash particulates are added.

RECOMMENDATIONS

Due to the opposing trend between the impact energy and other mechanical properties, the authors recommended that the percentage of CMSAp reinforcement should not exceed 15%. This is because at above 15 wt.% CMSAp additions, the impact energy may probably be too low to provide the needed impact energy for most engineering applications such as automotive and building applications.

THANK YOU FOR LISTENING
GOD BLESS YOU.