



The Characterization of the Microstructure and Interfacial Behaviour of Egg Shell Particulate Polyester Reinforced Composites Proposed for Dielectric Applications

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Abstract

This work investigated the polarizability of egg shell (ES) particulate composite using polyester resin as the binder. The egg shells were washed and dried after which they were milled into powder and sieved into sieve grade of 300 μm . The ES particles were varied from 10 to 50 wt.% composition. A mineralogical analysis carried out by the X-ray diffractometer revealed that the egg shell particles contain the following elements: C, O, Na, Mg, Al, Si, K and Ca. Surface morphology of the egg shell particles as revealed by the SEM confirmed the particles to be solid in nature. The TGA/DTA analysis shows that the ES particles are thermally stable. The properties tested and analyzed are: dielectric strength, dielectric constant, resistivity, moisture content and water absorption capacity. Better enhancement of property was obtained for the composites with lower filler loading for dielectric strength, dielectric constant and resistivity respectively. Their moisture contents and their water absorption capacities were relatively low, thus making them good candidate materials for electrical insulation both for indoor and outdoor applications. The measured polarizability was not too high compared to the standard values. However, their best performance will be limited to electrical insulation in low voltage applications.

1. Introduction

Dielectric means any insulating medium which intervenes between two conductors. It suggests the absence of conduction and describes materials which are not electrical conductors. Dielectric materials are employed in making capacitors, providing an insulating barrier between two conductors (as in cross over and multi-layered circuits). The study of dielectric properties concerns the storage and dissipation of electric and magnetic energy in materials. Dielectrics significantly explains various phenomena in electronics, optics, solid-state materials, and cell biophysics [1].

Although the term insulator implies low electrical conduction, dielectric typically means materials with a high polarizability. The latter is expressed by a number called the relative permittivity (also known as dielectric constant). The term insulator indicates electrical barrier while dielectric is used to depict the energy storing capacity of the material through the process of polarization. A common example of a dielectric is the electrically insulating material between the metallic plates of a capacitor. The polarization of the dielectric by the applied electric field increases the capacitor's surface charge for the given electric field strength. Dielectric materials are basically plain and simple electrical insulators. By the peripheral application of electrical field, these electrical insulators get polarized [1].

Dielectric materials can be used in capacitors for energy storage. It is used in photosensitive materials for charge storage in laser printers and copying machines. It is used for mechanical actuation, sound generation, piezoelectricity, cap sense etc.

In electrical and electronic industries, insulators that have good dielectric properties with other properties such as light weight, corrosion and wear resistance with relatively good mechanical properties are highly needed [2]. Some factors that determine the choice in chosen an insulator are the dielectric constant, dielectric strength, moisture content, water absorption etc. thus, for a material to be considered as a dielectric material (insulator), it must possess high values of dielectric strength, resistivity, dielectric constant and thermal insulation capacity [3]. The material should also be noted for its low water absorption and moisture content.

Agro waste materials (plant and animal waste) today are enormous. These agro-wastes are not of economic importance rather, they are detriment to the human system and the ecosystem as a whole if not properly disposed. Thus, agro-waste materials prove to be the cheapest among the different particulate reinforcement materials in use. Its comparative cost advantage, low composite density and improved properties have made it a novel material for composite production for improved dielectric and mechanical properties [4]. These led many researchers to find a way of converting agro-waste materials to useful product for mankind and to reduce environmental hazard through composite technology, e.g. agro-waste materials (like animal bone, egg shells, snail shell, orange peels, groundnut shells, etc.) are now used as substitute raw materials for composites production due to their environmental and economic advantages. This study therefore determined the dielectric polarizability of agro-waste products (egg shells). The availability of egg shell and its chemical composition makes it a potential source of filler in polymer matrix like polyester. An egg shell (ES) is the outer covering of a hard-shelled egg and of some forms of eggs with soft outer coats. i.e. eggshell forms the outer crust of an egg and it is a non-edible product with very limited use and value and is largely disposed of as a waste [5]. The egg is composed of a central yolk surrounded by the albumen (egg white), eggshell membranes, calcified eggshell and cuticle. Thickness is the main factor contributing to the mechanical strength of the eggshell [6].

Considering the high disposal task which further increases due to rise in egg usage by the growing populace and egg processing industry, it is necessary to find an alternative method which would convert the waste eggshells into a more valuable item; giving financial benefits to the egg processing industry and as well overcome environmental pollution [7, 8].

Composite materials are materials that are designed and made by blending two or more materials to achieve properties that are superior to those of their constituent materials. Polymer composites consist of a polyester resin as the matrix, with fibers/fillers as the reinforcing medium. Significant interest has been generated in the manufacture of thermoset composites due to their unique properties, which includes their good dielectric properties, mechanical properties, their thermal stability, and a reduced product cost. Due to the combination of more than one material, the properties of composites are influenced by many factors such as filler characteristics, filler content, and interfacial adhesion.

Increase in industrial and electrical activities have led to ever increasing demand for improvised materials, satisfying strict requirements like high strength, high modulus, improved dielectric strength, high dielectric constant, high resistivity, lower density, lower costs, light weight etc. Traditional materials often fail to achieve all these properties together and hence focus is shifting more towards composite materials. Design flexibility in composite materials allows use of constituents which work together to meet tough and challenging demands of modern engineering applications thus allowing their use in electrical and electronics industry, automobiles, marine, aeronautical, sports, and related applications [8].

Fiber–matrix interface influences the mechanical and dielectric performance of a composite other than the just the fiber or the matrix. It determines how well the matrix transfers the load to the fibers. Chemical and mechanical bonding may form the interface. In most cases however, more than one type of bonding occurs. Coupling agents are often added to form a chemical bond. Natural roughness of the fiber surface can cause interlocking to enforce a mechanical bond between the fiber and matrix. This can cause the behavior of filled polymers to be more complex than their unfilled counterpart. This project targeted using eggshell as the reinforcement with polyester as the matrix to produce polymer composite. Its dielectric properties which include dielectric strength, dielectric constant, and resistivity were tested in order to determine areas where it can be applied.

Hassan *et al* [9] carried out a research on Eggshell polyester particulate composites; eggshell particles were used as reinforcement in polyester matrix. 10 to 50 wt% eggshell particles at intervals of 10 wt% were added to polyester as reinforcement. The results showed that the mechanical properties of the polyester/eggshell particulate composite increased steadily with increasing eggshell addition. Hence the development of polyester/eggshell particulate composites material with good mechanical properties and light weight which is relevant to the electronics, auto and building industries has been achieved.

J. Senthil and P. Madan Raj [10], presented an article on the mechanical properties and water absorption of egg shell polymer composites as a function of egg shell powder to be tested. Parameters such as tensile strength, tensile modulus, elongation at break and flexural test were carried out on the prepared samples. It was found that the addition of egg shell powder to the polymer led to decrease in the tensile strength, modulus of elasticity, hardness on other hand it increases the % elongation at break and flexural strength. Water absorption of the composites increased by increasing the wt.% of egg shell.

Omah *et al* [11] studied the dielectric properties of composite materials developed from carbonized and uncarbonized agro-waste (cow bone) material. The results show that smaller particles and weight percentage have the best properties.

Suhas *et al* [8], explored the potential of chicken egg shell as a filler material in E-glass/epoxy composites. Chicken egg shell was treated with sodium chloride solution and then dried, pulverized and sieved to 150 μ m particle size to get egg shell fillers. The composite panels were produced and tested for tensile and impact strength. Results showed drop in tensile strength while tensile modulus and impact strength increased with inclusion of egg shell fillers.

2. Methodology

2.1 Sourcing and preparation of materials

Egg shells (ES) were locally sourced from Nsukka vicinity and processed into powder; Cobalt Napthanate (accelerator), Methyl Ethyl Ketone Peroxide (catalyst) and Polyester (matrix) which has a melt flow index of 2.5 - 3.5 g/min, and density, 0.926 g/cm³, were used as purchased from a Chemical vendor at Enugu.

The eggshells as earlier mentioned were locally sourced from local food restaurants in Nsukka of Enugu State. They were washed and sun-dried for one week, after which it was pulverized and screened to 300 μ m particle size. The ES in various weight fractions (10wt% - 50wt%) were then blended with the resin with 0.1% catalyst and accelerator, and were vigorously stirred to ensure an efficient and proper coating of the reinforcing particles. For every 100wt% of the composite composition, the ratio of the polyester to fibre was 9:1, 4:1; 7:3; 3:2 and 1:1. The produced composites were subjected to the different dielectric property tests. The pictorial image of the egg shells, composite samples and their moulds are shown in [Figures 1 and 2](#)



Figure 1a. Dried ES particles



Figure 1b. Ground ES particles



Figure 2a. Composite samples



Figure 2b. Composites moulds

2.2 Experiments

Dielectric strength was determined in kV/mm using 50 kV Foster alternating current dielectric testing machine. Cylindrical specimens of 18 mm diameter and 105 mm length were placed between two 10 mm diameter copper ball electrodes and the system containing the sample was covered with glass shield to prevent a splashing out from the sample due to surface flashover. The test voltage was applied across two ball-typed electrodes and was increased until the specimen failed at a given voltage. The failure was characterized by smoking.

The dielectric constant of the composite samples was determined by moulding rectangular plates of length 50 mm, width 30 mm and thickness 2 mm. An air gap was created between the two parallel plate capacitors with same thickness as the composite sample. The parallel plate capacitors were connected to the battery and the voltage across was measured (V_o). The samples were then used separately to fill the air gap between the capacitor plates that are connected to a battery and the voltage (V) across was also measured differently for each of the composite samples.

Resistivity test (Kaise insulation test model SK5010) which was measured as the insulation resistance, gave the resistance of the specimen to the flow of electric current. The samples were moulded into cylindrical shapes of diameter 18 mm and length 105 mm with a copper wire of diameter 2.5 mm and length 5 mm placed at the ends of each sample.

The water absorption capacity and moisture content of the samples were measured by immersing the samples in water for a period of one day and then palmed dried with a cloth, and weighed to the nearest 0.0001g. The weights (M_1) and (M_2) of the samples were measured before and after the absorption and after drying process respectively. For the moisture content, the samples were placed in the oven at a temperature of 105 °C and their weights measured at an interval of an hour until a constant mass (M_3) was obtained.

2.3 Product characterisation

TGA (SDT Q600 V20.9) was carried out on the samples of size 6.2520mg to determine the degradation temperature and thermal stability of the material. All the samples were scanned from 50 °C to 1000 °C at a heating rate of 20 °C/min under N_2/O_2 . XRD measurements were carried out on the

samples between 0 to 90 degrees 2θ. It was used to carry out a mineralogical analysis to reveal the elements present in the material. The Scanning electron microscope (SEM JEOL JSM-6480LV) was used in studying the micrographs of the composite samples with 10%, 30% and 50% egg shell reinforcement; and the elemental compositions measured using EDS.

3. Results and Discussion

3.1 Dielectric strength

The result of Figure 3 showed a plot of dielectric strength (kV/mm) versus weight % of egg shell reinforcement. It was observed that the dielectric strength values increased as the filler wt.% increased but decreased after exceeding 40wt%. This was because smaller wt.% enhances better wettability between the reinforcement and the matrix, thus better bonding and better property; however, the interfacial bonding between the particulate and the resin got weaker after the 40wt% reinforcement, thus reduced property. This is in agreement with the work of other researchers. [12].

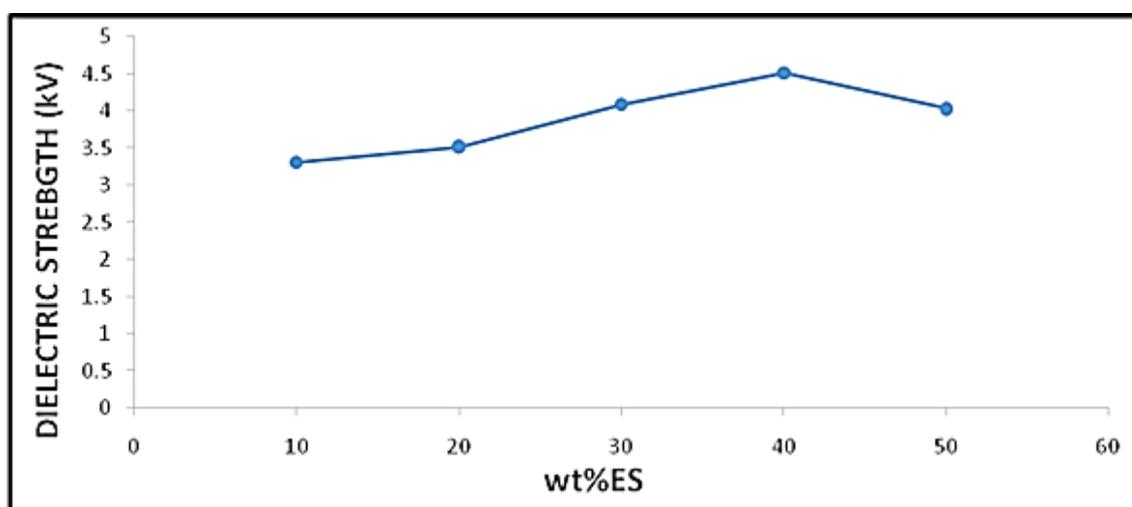


Figure 3. Dielectric strength of ES Polyester Composite

3.2 Dielectric constant

The permittivity of a material (ϵ) which is related to the dielectric constant (ϵ_r), expresses the ability of a material to polarize in response to an applied field. Thus, the greater the polarization by a material in an applied field of given strength, the greater the dielectric constant. The dielectric constant (ϵ_r) was estimated by considering the voltage across parallel plate capacitor with an air gap (V_0) and the voltage across the parallel plate capacitor with the composite sample in between them (V) using Eqn. 1

$$\epsilon_r = \frac{V_0}{V}$$

Eqn. 1

Figure 4 shows a graph of dielectric constant against wt% ES. Increase in filler wt.% increased the tendencies of porosity in the material, thus, decreased polarizability. The dielectric constant of the composites was therefore observed to decrease with increasing filler loading. This is because the presence of free volume in the form of pores results in a decrease in dielectric constant as the relative permittivity of air is about one [13]. This is in agreement with the work done by Jie Xet-al [14]. The small grain size (300 μm) of ES used enhanced the materials dielectric constant due to numerous number of polarized dipoles that orients due to applied electric field.

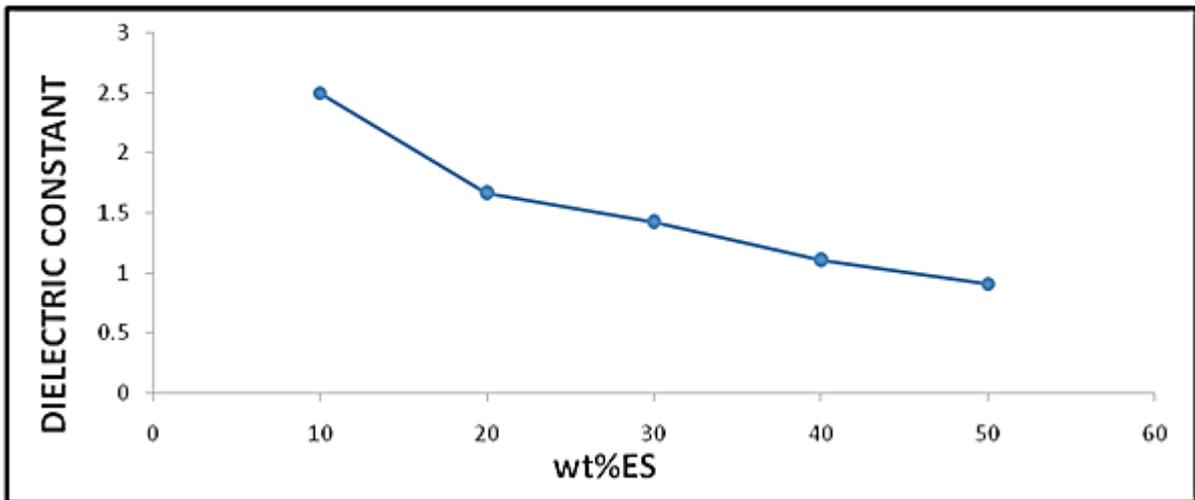


Figure 4. Dielectric constant of ES polyester composite

3.3 Resistivity

Resistivity values as seen in **Figure 5** increased as the percentage of filler loading was increased but decreased after exceeding 30wt%. This is because at lower filler loading, there was high loosed polymer layers which possibly permits the transport of free electrons through the bulk of the material, thereby supporting electrical conductivity, thus, low material resistivity; but at increased filler loading, the particles become heavily compacted and perhaps obstruct the movement of free electrons thereby enhancing the resistivity of the composite material. Moreso, at smaller wt.%, particles dispersed evenly in the matrix which improved the interfacial bonding between the reinforcement and the matrix, thus enhanced property; but particle – matrix interfacial bonding got weaker after the 30wt% reinforcement due to insufficient resin for bonding thereby decreasing the resistivity of the composites. This is in agreement with the work of other researchers [12].

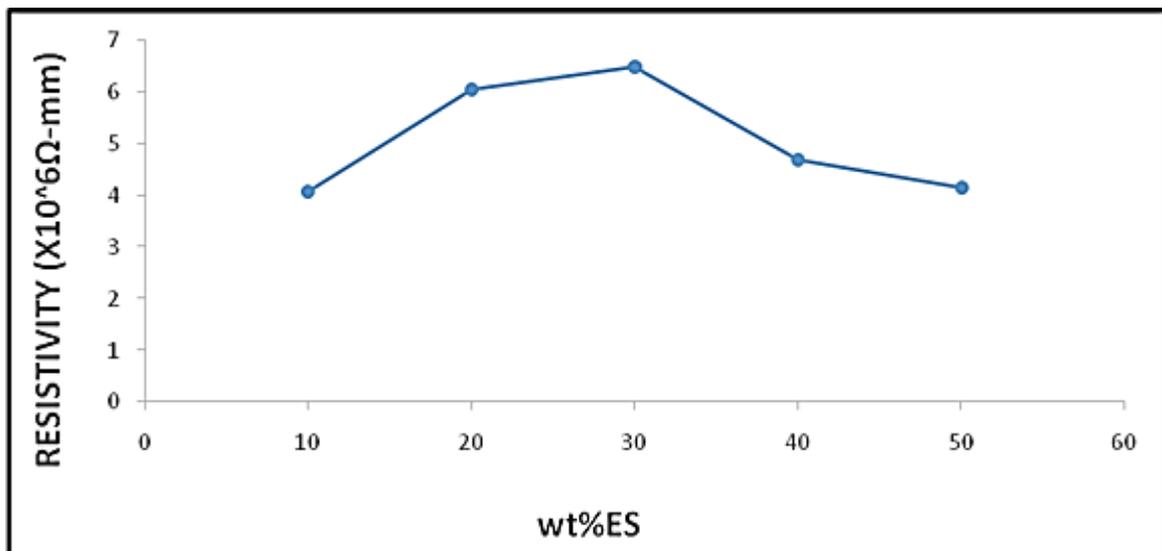


Figure 5. Resistivity of ES Polyester Composite

3.4 Determination of water absorption and moisture content

The water absorbed (W_A) was calculated as percentage weight gain using equation 2 below according ASTM D570-98 [15].

$$W_A = \frac{M_2 - M_1}{M_2} \times 100 \quad \text{Eqn. 2}$$

The moisture content (M_C) was calculated as percentage of the dry sample from equation 3:

$$M_C = \frac{M_1 - M_3}{M_1} \times 100 \quad \text{Eqn. 3}$$

Figure 6 shows the water absorption capacity/moisture content with increasing wt% of ES. The ES being polar in nature due to dirt absorbed more amount of water as the filler content increased. Moreso, with increased filler loading, there existed poor interfacial bonding between the filler and the matrix; this poor particle – matrix interfacial bonding resulted in an increase in the number of voids, causing increased water absorption [16, 17]. The moisture content of the samples increased with increase in wt.%. This was because more composition of the samples contained more internally and chemically bound water.

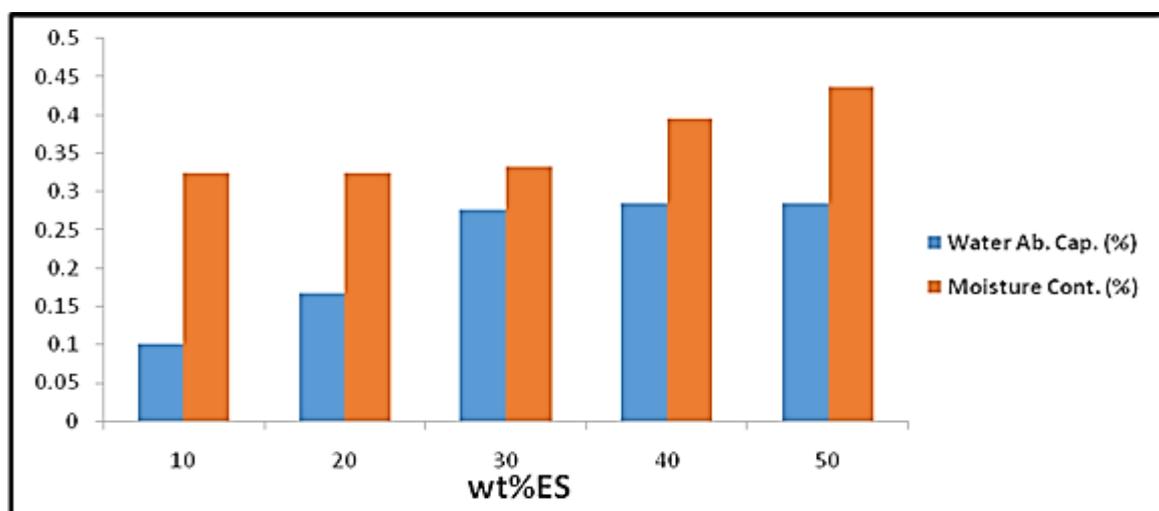


Figure 6. The Water Absorption Capacity and Moisture Content of ES Polyester Composite

3.5 Thermo-gravimetric analysis (TGA)

Thermogravimetric analysis carried out on the ES powder revealed information about the physical and chemical properties of the ES, measured as a function of increasing temperature with constant heating rate. The data collected on the SnS are shown in Figure 7. There are three areas of major weight changes in the TGA graph. The first occurred between 50°C and 200 °C which was due to the vaporization of water from the ES particles. There was a sharp decrease in the thermal stability of the ES particle between 200°C and 350°C. Thus, the degradation of the particles commenced precisely after 200°C for the ES. This is the second phase where some of the water and other cellulose content of the ES got burnt off. The thermal stability after this temperature maintained a slow decrease i.e. from 500°C until final degradation occurred at precisely 800°C. This is the third stage which is the point of termination of the experiment.

3.6 X – Ray Diffraction Analysis

The x – ray diffraction analysis carried out on the ES powder provided the following information about the structure of the crystalline materials and the phases present in the eggshell powder. The XRD pattern of the ES shown in Figure 8 revealed that the phases present were: silicon dioxide (SiO_2), Dolomite $\text{CaMg}(\text{CO}_3)_2$, Diopside, aluminian, syn $\text{Ca}(\text{Mg},\text{Al})$ and $(\text{Si},\text{Al})_2\text{O}_6$.; these phases have the following scores 48, 21, 19 and 16, with scale factors of 0.743, 0.432, 0.236 and 0.232.

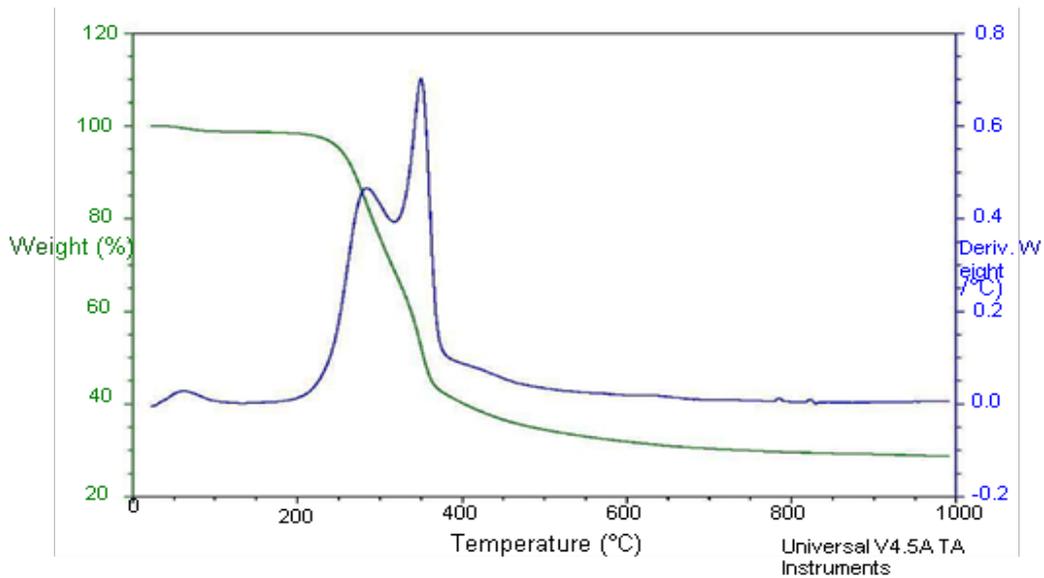


Figure 7. Thermo-gravimetric analysis (TGA) of ES polyester composite

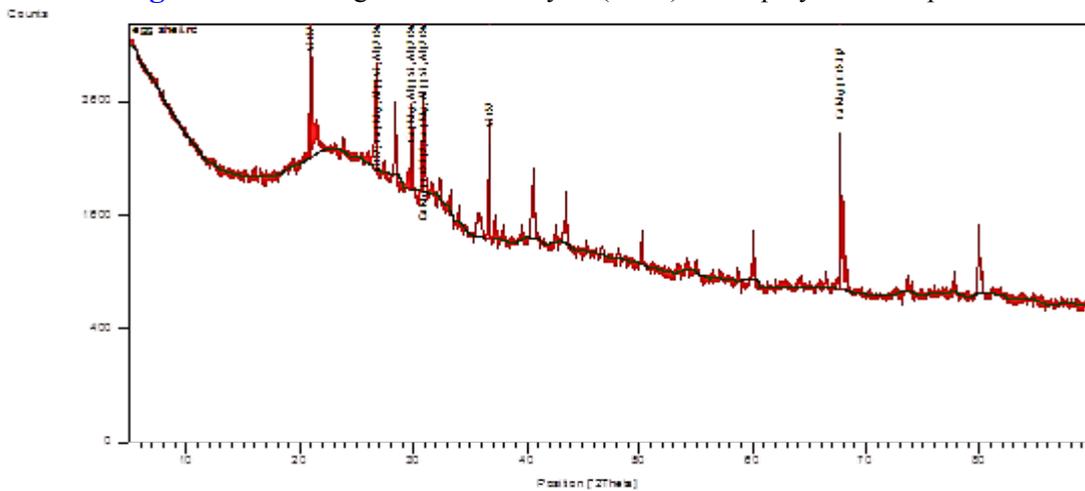


Figure 8. X-ray diffraction pattern of ES powder.

Table 1. Identified Patterns List of the XRD Peaks

Visible	Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
*	85-0794	48	Silicon Oxide	0.743	SiO ₂
*	74-1687	21	Dolomite	0.432	CaMg(CO ₃) ₂
*	05-0622	19	Dolomite	0.236	CaMg(CO ₃) ₂
*	25-0154	16	Diopside, aluminian, syn	0.232	Ca(Mg,Al) (Si,Al) ₂ O ₆

These represent the relative amount of each phase in the XRD pattern displayed in [Figure 8](#) and [Table 1](#). SiO₂ has the highest amount with a score of 48 and a scale factor of 0.743. Agro-based materials commonly have one or more of these elements: Si, Ca, C, Na, K, Mg, Al, and O; and their presence in the developed composites is seen in the phases of the XRD peaks and SEM/EDS scan results of [Figures 9 – 11](#) which showed the elemental compositions of the ES particulates, and revealed that aluminum, carbon, oxygen, calcium, nickel and silicon are the key constituent elements present. The XRD shows that the ES is void of harmful elements.

3.7 SEM/EDS

The SEM micrograph and the EDS graphs of the 10 wt%, 30 wt% and 50 wt% composite as shown in **Figures 9 – 11** revealed the particle nature of the ES i.e. the sizes and shapes of the particles; the reinforcements are solid particles and are randomly distributed.

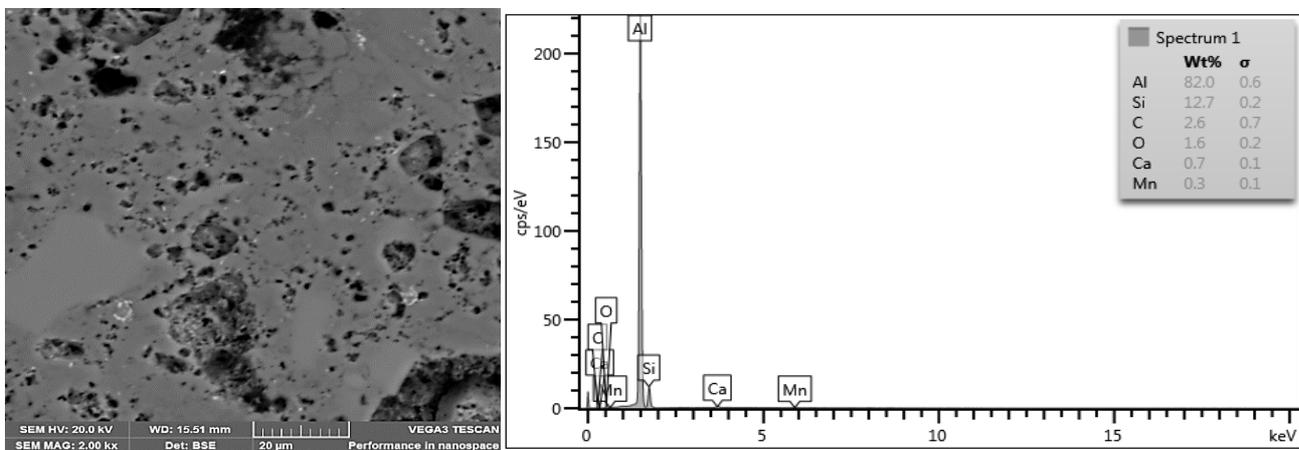


Figure 9. SEM/EDS of 10 wt% ES polyester composite.

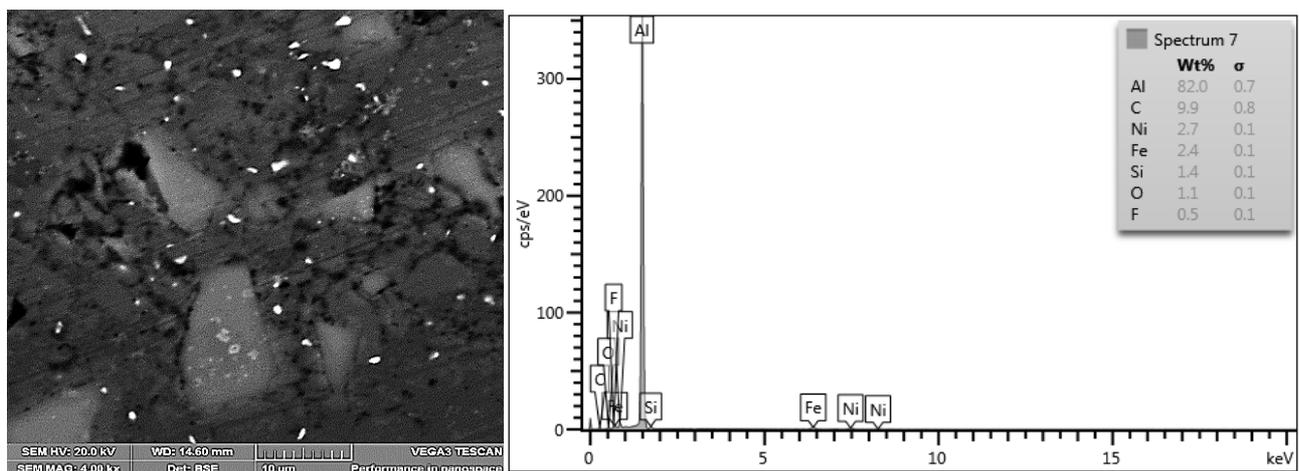


Figure 10. SEM/EDS of 30 wt% ES polyester composite.

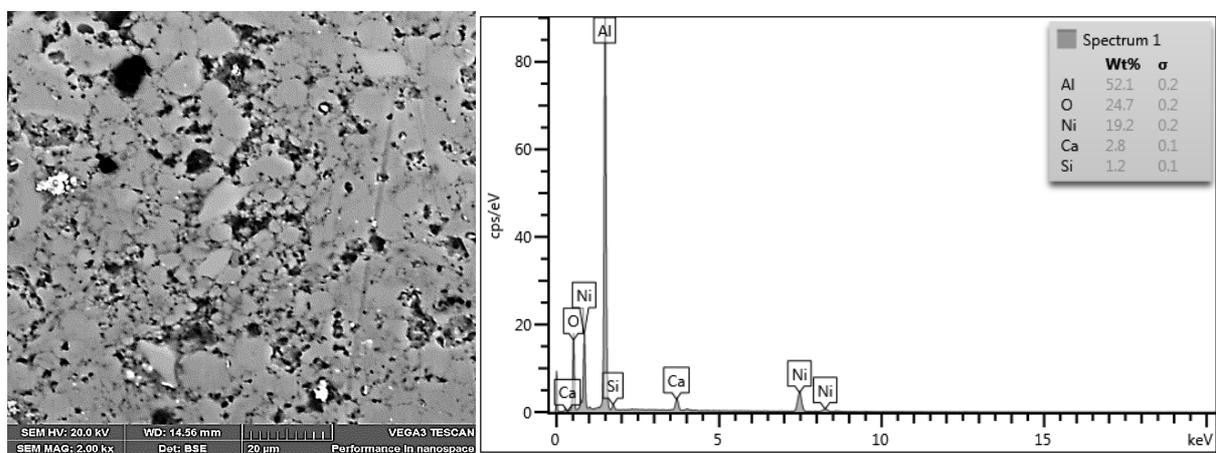


Figure 11. SEM/EDS of 50 wt% ES polyester composite.

The micrographs show the particles in white while the polyester resin is dark in colour; the white patches increased with increase in SnS particles. The elemental compositions of the ES particulates revealed that aluminum is the major constituent present as shown in the EDS scan of **Figures 9 – 11**. There are also high traces of other significant elements present like: oxygen, carbon, calcium, silicon, iron, and nickel. The EDS analysis also revealed that the ES particles did not contain radioactive elements that could be detrimental to the human body. It was also observed that the interlaminar structure of the eggshell polyester composite decreases as the volume of eggshell particles increases []. The jagged surfaced particles had more surface area for interaction with the matrix thus, good particle – matrix interfacial strength for enhanced dielectric properties. The SEM/EDS for 30 wt% and 50 wt% revealed the presence of more particles than that of 10 wt%.

Conclusions

This research work centered on the development and characterization of polymer matrix (polyester) containing different volume fractions of eggshell particles. From the above results and discussion, the following can be inferred:

1. The moisture content and water absorption capacity of the ES polyester composite is minimal thereby making the produced composites a candidate material for capacitors and good electrical insulators.
2. The dielectric strength, dielectric constant and resistivity of the composites had their prime values at 40wt%, 10wt% and 30wt% ES addition; thus, lower wt.% fillers enhanced the composite properties.
3. The dielectric constants of the ES polyester composite are low (less than ten) when compared with some conventional insulators, thus they can find application as insulation materials.
4. TGA analysis of the ES powder showed that it has high thermal stability and it can withstand a temperature as high as 800°C before being burnt off. Thus, the ES composites can be used in both indoor and outdoor applications where high temperature is needed.
5. The XRD confirmed that ES belongs to calcium family and that ES does not contain any radioactive element, therefore it is safe for composite production.
6. The small particle size of 300 µm used, improved particle – matrix interfacial bonding thereby minimizing the presence of inter – particle pores that would have been a good site for defects, thus, poor composites properties.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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