ASSESSMENT OF THE INFLUENCE OF PERIWINKLE SHELLPOWDER ON SOME MECHANICAL AND DIELECTRIC PROPERTIES OF EPOXY RESIN

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JULY, 2021

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P14SCPY8016/P17PSPY8114

**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES,
AHMADU BELLO UNIVERSITY ZARIA,
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF
MASTER OF SCIENCE (M.Sc.) DEGREE IN PHYSICS**

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JULY, 2021

Declaration

I declare that this dissertation titled “ASSESSMENT OF THE INFLUENCE OF PERIWINKLE SHELL POWDER ON SOME MECHANICAL AND DIELECTRIC PROPERTIES OF EPOXY RESIN” was carried out by me in the Department of Physics Ahmadu Bello University Zaria under the supervision of Dr. A.AAbdelmalik and Prof .U. Sadiq. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at any university.

Sadiq Abdulrahman _____ _____

Signature **Date**

Certification

The dissertation titled "ASSESSMENT OF THE INFLUENCE OF PERIWINKLE SHELL POWDER ON SOME MECHANICAL AND DIELECTRIC PROPERTIES OF EPOXY RESIN" by Sadiq Abdulrahman meets the regulations governing the award of master of science (M.Sc) degree of the Ahmadu Bello university, Zaria and is approved for its contribution to knowledge and literary presentation,

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Dedication

This project is dedicated to my wife, Mrs. Serifat Abdulrahman and my sister, Mrs. SalamatAliyu, for cherishing me and giving me the right advices.

Acknowledgement

All praise be to Almighty Allah for making it possible for me to successfully complete this work.

My profound and deepest gratitude goes to my supervisor, Dr.A.A.Abdelmalik for guiding and standing by me despite his tight schedules. I will also like to express my gratitude to my minor supervisor, Prof. U. Sadiq, for his guidance and support. May the Almighty Allah continue to guide, protect and grant you good health.

I am deeply indebted to Prof. M. Abdulwahab of the Department of Metallurgical and Materials Engineering, ABU Zaria for the financial assistance given to me during the course of the practical works. My gratitude also goes to Mal. Faruq Tambuwal and Mal. Ado for their financial assistance in the preparation of this dissertation.My appreciation also goes to Mal. Muhammad Dabai and Mal. Nuhathe laboratory Technician in the Department of Physics for their assistance during the course of the practical work.

I will also wish to thank my friends, Mal. AbdulfataiUsman, Mal. Bashir, and Mal. B. Ibrahim and other staff of the Department for being there for me.

Lastly I am indeed grateful to my wife, sister and family for their support and encouragement.

Abstract

Composite insulators with metal oxides are widely used in overhead transmission. While synthesized metal oxides are often used in polymer composites, efforts are on to develop metal oxide micro/nanoparticles from naturally occurring materials. The consumption of periwinkles, a species of small edible sea snail produces residual shells that aredisposed of. The shell, a natural ceramics containing several metal oxides is used in material application such as concrete. This research report the characteristics of a powder produced from the periwinkleshell (PWS) and its effect on the mechanical and dielectric behaviour of epoxy-based polymer composite. The sizes of the particles of the prepared shell fine powder were estimated using the Scanning Electron Microscopy and the image revealed that the sizes of the PWS powder range from 4.39 to 100μm. The chemical composition, thermal conductivity, anddielectric properties were studied using the X-ray Fluorescence (XRF), Thermal conductivity setup, and programmable LCR Bridge respectively. Polymer composite was produced from epoxy resin and the prepared PWS as filler with a composition ranging from 0.5 – 1%. The dielectric and mechanical properties of the produced epoxy composite samples were studied using the programmable LCR Bridge, Monsanto tensometer, Vickers harder tester, and Charpy impact testing machine. The XRF result revealed a powder with over 80% CaO. The thermal and electrical conducting properties of the powder were superior compared with that of pure CaO. The dielectric constant and the electrical conductivity of the powder were determined to be 12.15 and 1.6876×10^{-8} S/m respectively, at the frequency of 200 Hz. Improved properties of epoxy composites were achieved using PWS as reinforcement up to a maximum of 1wt%. The dispersion of the powder up to 1wt% results in a decrease in the dielectric loss and an increase in the dielectric constant of the epoxy polymer. The mechanical properties have optimum improvement of up to 68% with the dispersion of 0.9wt% of PWS into the epoxy polymer. Periwinkle shell powder, if properly processed to micro and even nano-sized particles, can be good candidate filler in polymer composites. The waste periwinkle shell can serve as a cheap resource to produce low-cost polymer composite with improved insulation properties for use in high voltage application and encapsulation power electronic modules.

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Abbreviation

PWS	-	Periwinkle Shell
%	-	Percentage
δ	-	Delta
μm-	Micrometer	
Kgm^{-3}	-	Kilogram per Meter Cubic
SEM	-	Scanning Electron Microscope
LCR	-	Inductance Capacitance Resistance
XRF	-	X-ray Fluorescence
Kv	-	Kilovolt
mm	-	Millimeter
mA	-	Miliampere
J	-	Joule
Kev	-	Kilo Electron Volt
$Wm^{-1}k^{-1}$	-	Watt per Meter per Kelvin
Mpa	-	Mega Pascal
KHz	-	Kilo Hertz
Sm^{-1}	-	Siemens per Meter
^{0}C	-	Degree Celsius
DC	-	Direct Current
AC	-	Alternative Current

Pb	-	Lead
CaO	-	Calcium Oxide
SiO_2	-	Silicon Oxide
MgO	-	Magnesium Oxide
Cr_2O_3	-	Chromium Oxide
Fe_2O_3	-	Iron Oxide
K_2O	-	Potassium Oxide
Na_2O	-	Sodium Oxide
MnO	-	Manganese Oxide
ZnO	-	Zinc Oxide
CuO	-	Copper Oxide
Al_2O_3	-	Aluminum Oxide
P_2O_5	-	Phosphorus Oxide
SO_3	-	Sulfur Oxide
Cl	-	Chlorine
SrO	-	Strontium Oxide

CHAPTER ONE

INTRODUCTION

1.0 BACKGROUND OFTHE STUDY

The need for improved polymeric insulation brings about the idea of composite dielectrics. This involved the addition of micro/nano-additives in dielectric materials to create composite materials. Composite materials are multiphase materials in which the phase distribution and geometry have been controlled in order to optimize one or more properties. The intent of producing composite material is to make a material that combines the best properties. Several papers have reported progress made in the dispersion of additives in polymers to produce the composite dielectric materials (Singha and Thomas, 2008). Polymeric materials are important components of electrical insulation and epoxy family occupies a very important position in polymeric materials.

Epoxies are class of thermostat materials used extensively in structural and specialty composite applications because they offer a unique combination of properties that are unattainable with other thermoset resins. Available in a wide variety of physical forms, from low viscosity liquid to high melting solids, they are amendable to a wide range of processes and applications. Epoxies offer high strength, low shrinkage, excellent adhesion to various substrates, effective electrical insulation, chemical and solvent resistance, low cost and low toxicity.

They are easily cured without the evolution of volatiles or byproducts by a broad range of chemical species. Epoxy resins are also chemically compatible with most substrates and tend to wet surfaces easily making them especially well-suited to the composite application (Boyle and Martin, 2001). In an attempt to improve the mechanical properties of the epoxy polymer, the effect of different fillers dispersed in the polymer was investigated by various researchers.The

effect of periwinkle shell powder on the mechanical properties of polypropylene and polyester composites was studied at high filler content (10-50 wt %) (Onueghu and Igwe, 2011). It was reported that the addition of the filler in the polypropylene matrix led to an improvement in the mechanical properties of the polypropylene composite and that the composite can broaden the application scope of polypropylene. The addition of 30 wt% periwinkle shell in polyester was reported to have produced a polyester composite with the highest tensile and flexural strength (Onyechi and Asiegbu, 2015). For polymer composite used as polymeric insulation, oxides of metals are often used as fillers at low filler content. Aside from acting as insulators, polymers serve as a mechanical support in the power system.

Polymer nanocomposites were found to have improved the dielectric loss and breakdown strength at certain filler content. Some of the common metal oxides used to modify the structure of the polymer matrix include SiO_2, TiO_2 and Al_3O_2(Liang and Wong, 2017). While the microparticles of these metal oxides produced materials with increased dielectric loss, the nanoparticles were found to produce polymer composites with decreasing dielectric loss at lower filler loading. This was attributed to the morphology of the nano-materials (Singha and Thomas, 2008).

Calcium oxide as an alkaline earth metal oxide is known to have many applications. This includes its use as catalyst (Ngamcharussrivichai and Meechan, 2011), toxic-waste remediation agent, an additive in refractory (Tang and Claveau, 2008),and a crucial factor for CO_2 capture (Park and Bae, 2013). Calcium oxidealso been used as an additive to modify the electrical and dielectric properties of materialscomposite (Alavi and Morsali, 2010).Report on the electrical properties of calcium oxide shows that, it has electrical conductivity of $1 \times 10{-}6$ S m−1 (Surplice, 1966). The electrical conductivity of polyaniline (PANI) nanofibers was studied by

systematically varying the addition of CaO in the range from 0.005 to 1.00 g. Increase in CaO loadings was reported to have resulted in a decrease in the electrical conductivity of the composite material (Rahman and Wee, 2014).

Animal shells are known to be composed of several metal oxides that are being exploited for numerous industrial applications. Instead of producing micro- or nanoparticle through chemical methods, can the micro- or nanoparticles produced from such waste sea animal shells serve the same purpose? Periwinkle is another type of seashell animal. It is a species of small edible sea snail that is consumed in large quantity in Nigeria. Its consumption produces residual shells which posed an environmental hazard. The shell is a natural ceramics which contained several metal oxides used in material applications such as filler in concrete production. The shell ash was investigated as a replacement for cement in concrete. These shells are used as a mechanical re-enforcement (Raju, 2012). It was utilized as coarse aggregate in concrete in areas where there are neither stones nor granite for purposes such as paving of water logged areas. The large amount of these shells are still disposed off as waste and with disposal already constituting a problem in areas where they cannot find any use for it, and large deposits have accumulated in many places over the years (Raju, 2012).

It was a reported that there are about 40.3 tones of Periwinkle per year being harvested from 35 mangrove communities of Delta and River states of Nigeria (Jamabo and Chinda, 2010). Massive periwinkle harvesting is also reported from some communities in Bayelsa, Cross Rivers and Edo States of Nigeria (Jamabo and Chinda, 2010). According to Aku (2012), Periwinkle shell particle exhibited a density of 1.24g/cm^3. Structurally, the periwinkle shell has several layers and is typically made of an organic matrix (Conchiolin) which is bonded with calcium carbonate precipitate, carbonate-filled organic matrix shells are resistant to water and this

property makes it possible for periwinkle shells and their derivatives to have very wide applications such as, it is used in enhancing microbial breakdown of spilled oil and also as coarse aggregates in concrete (Painter and Hemmer, 1979).It can be used for removal of Pb and Cu from industrial waste and loss control agent in water-based drilling mud (Powell and Hart, 1985). In this work, microparticles prepared from waste periwinkle shells are characterized for its possible use in polymer composite for mechanical properties and high-voltage electrical insulation application.

1.1 PERIWINKLE SHELL

Periwinkle is a species of small edible whelk or sea snail, a marinegastropodmollusc that hasgills and an operculum, and is classified within the family ofLittorinidae, Periwinkles are robust intertidal species with a dark and sometimes banded shell. It is native to the rocky shores of the Northeastern coasts of the Atlantic Ocean (Welch, 2010).

The periwinkle shell (PWS) is broadly ovate, thick, and sharply pointed except when eroded. The periwinkle shell contains six to seven whorls with some fine threads and wrinkles; the color is variable from grayish to gray-brown, often with dark spiral bands. The base of the columella is white, the periwinkle shell lacks an umbilicus, the white outer lip is sometimes checkered with brown patches and the inside of the shell has a chocolate-brown color (David and Gofas, 2011). Benson (2008), reported that, the width of the periwinkle shell ranges from 10 to 12 mm at maturity, with an average length of 16–38 mm and height can reach up to 30 mm, 43 mm or 52 mm. Periwinkles shell is used as bait for catching small fish, it is usually crushed and the soft parts extracted and put on a hook (Painter and Hemmer, 1979). A sample picture of these Periwinkle shells (PWS) is shown in PlateI



Plate I. Periwinkle shells

1.2 EPOXY RESIN

Epoxy is a term used for both the basic components and the cured end products of epoxy resins, as well as a colloquial name for the epoxide functional group. Epoxy has a wide range of applications, including metal coatings (Hakiki,2015), used in electronics and electrical components and high tension electrical insulators (Clayton, 1987), fiber-reinforced plastic materials and structural adhesives (Hakiki, 2015).

Epoxy resins (polyepoxides) are a class of reactive pre-polymers and polymers which contain epoxide groups. Epoxy resins may be reacted either with themselves through catalytic homopolymerization or with a wide range of co-reactants including poly-functional amines, acids, phenols, alcohols and thiols. These co-reactants are referred to as hardeners or curatives and the cross-linking reaction is commonly referred to as curing. Reaction of epoxy resin with

themselves or with poly-functional hardeners forms a thermosettingpolymer, with high mechanical properties, temperature and chemical resistance (Farizal, 2015). TheStructure of a cured Epoxy resin is shown in Figure 1.1.

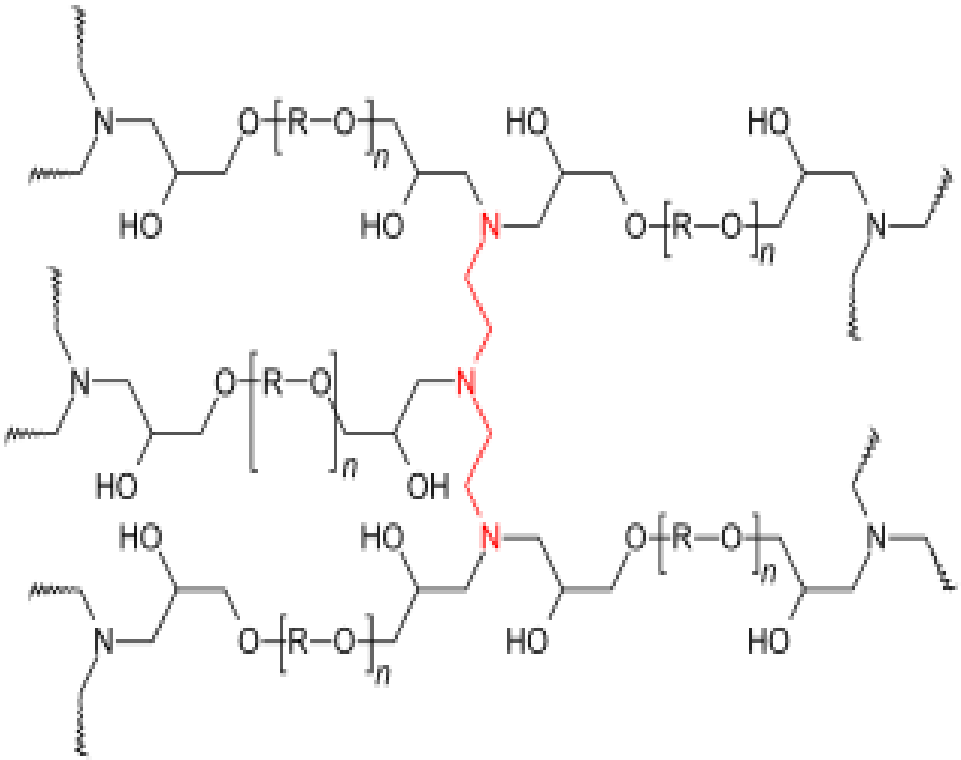


Figure 1.1. Structure of Epoxy resin (Farizal, 2015)

The triamine hardener is shown in yellow, the resin in white, the resin's epoxide groups have reacted with the hardener and are not present anymore. The material is highly cross-linked and contains many OH groups, which confer adhesive properties. Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups; common types of epoxy resin are bisphenol A, bisphenol F, Novolae, Aliphatic and Glycdylamine. A wide range of epoxy resins are produced industrially, the raw materials for epoxy resin production are today largely petroleum derived, although some plant derived sources

are now becoming commercially available and epoxy resins are polymeric or semi-polymeric materials (Hakiki, 2015).

An important criterion for epoxy resins is the epoxide content, the epoxide number, which is the number of epoxide equivalents in 1 kg of resin or as the equivalent weight, which is the weight in grammes of resin containing 1 mole equivalent of epoxide (g/mol).

The equivalent weight or epoxide number is used to calculate the amount of co-reactant (hardener) to use when curing epoxy resins. As with other classes of thermoset polymer materials, blending different grades of epoxy resin, as well as use of additives, plasticizers or fillers is common to achieve the desired processing, final properties and to reduce cost (Staubli, 1963).

1.2.1 COMPONENT OF EPOXY RESIN

Uncured epoxy resins have poor mechanical, chemical and heat resistance properties,good properties are obtained by reacting the linear epoxy resin with suitable curatives to form three-dimensional cross-linked thermoset structures. This process is commonly referred to as curing or gelation process, Curing of epoxy resins is an exothermic reaction and in some cases produces sufficient heat to cause thermal degradation, if not controlled. The resin and hardener are supplied pre-mixed to the end user and only require heat to initiate curing. There are two basic components of the epoxy resin namely;

i. Resin: the resin component is usually light, sometimes almost clear colored and odorless.Examples are diepoxide and polyepoxide.
ii. Hardener: the hardener component is usually dark and has slight odor.Examples are Polyamides, mercaptans, phenolic.

When these two components are mixed, they chemically bond together and once the chemical reaction has finished, it is strong and rigid plastic material. Epoxy resins are used because of their outstanding chemical resistance, durability, low porosity and strong bond (Farizal, 2015).

1.3 COMPOSITE

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. Composites are made up of individual materials referred to as constituent materials. There are two main categories of constituent materials: matrix and reinforcement.

The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties (Waterman, 2007). More recently, researchers have also begun to actively include sensing, actuation, computation and communication into composites, which are known as Robotic Materials.

Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, race car bodies, shower stalls, bathtubs, storage tanks, imitation granite,andcultured marblesinks and countertops. The most advanced examples perform routinely on spacecraft and aircraft in demanding environments (Waterman, 2007). Sample pictures of these composite are shown in Figure 1.2.

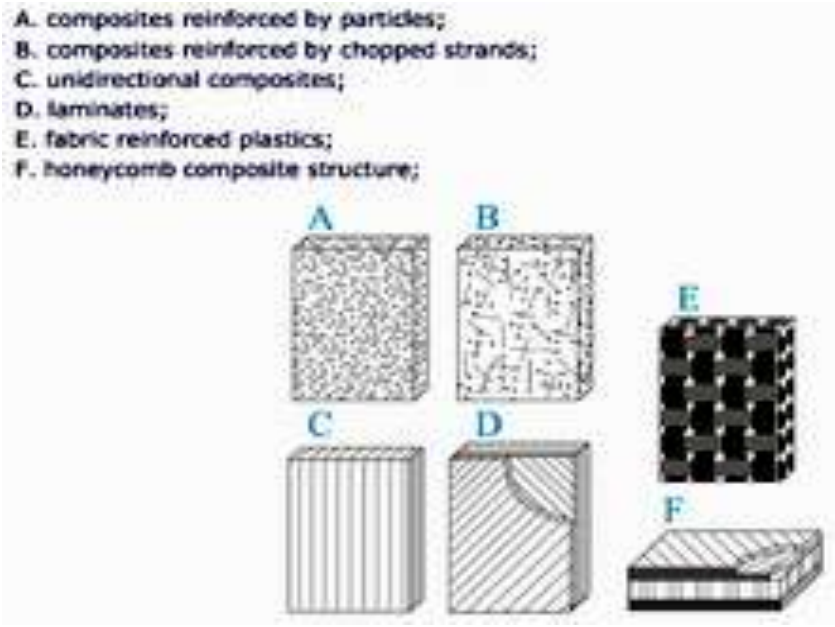


Figure 1.2. Structure of composite in different constituent materials (Waterman, 2007).

1.4 STATEMENT OF RESEARCH PROBLEM

Some natural ceramic sources such as clays, animal shells etc, for a long period of time have been used for industrial polymeric insulation in some part of the world. In Nigeria, these natural ceramic sources are in abundance and these shells are still disposed off as waste and with disposal already constituting a problem in areas where they cannot find any use for it. However, the application of these shells has not been explored in industry for high voltage insulation. In line with this, this research work intended to examine the feasibility of using periwinkle shells powder to enable waste to be converted to wealth.

1.5 AIM AND OBJECTIVES

The aim of this research is to investigate assessment of the influence of periwinkle shell powder on themechanical and dielectric properties of Epoxy resin.

The objectives of the research are to:

i. Produce powder from properly cleaned periwinkle shell; perform the morphology,

electrical and thermal characterization of the powder to understand the properties of the particles.

ii. Prepare an epoxy resin based micro polymer using the powder obtained from periwinkle shell.

iii. Examine the impact of the powder on the mechanical strength of the micro-polymer.

iv. Evaluate the dielectric properties of the prepared micro-polymeric insulation.

v. Compare the measured properties of the polymer samples with dispersed periwinkle shell powder.

1.6 SCOPE OF THE WORK

In this research work,microparticles powder was produced from periwinkle shell with particle sizes ranging from 4.39 μm to 100 μm size. Polymer composite was successfully prepared from epoxy resin and the periwinkle shell powder with enhanced properties.The prepared samples were subjected tomorphology, elemental analysis and thermal conductivity, mechanical and dielectric characterization.

1.7 JUSTIFICATION

Periwinkles which are naturally found at the coasts of Atlantic Ocean are a species of small edible sea animal. Periwinkles are used as good seafood. The natural ceramic sources are of recent considered as valuable sources for numerous industrial applications. Sequel to this proper utilization of these natural ceramic sources as polymeric will add economical value and at same reduce disposal challenges in the environment.

CHAPTER TWO

LITERATURE REVIEW

2.0 INTRODUCTION

Various studies on composite and periwinkle shell have been carried out by many researchers in the past. This chapter reviews the literatures, which will give foundation for this work as basis for the better understanding of the topic and also as a guideline for this thesis. The major focus of the study is on the properties of polymeric insulation from periwinkle shell as dielectric material, mechanical properties, its preparation, characterization of dielectric and its application to power industry.

2.1 REVIEW OF PREVIOUS WORK

Onyechi and Asiegbu (2015), carried out work on effects of particle size of periwinkle shells (PWS) on the mechanical properties of particulate reinforced polyester composite and they considered particle sizes of 400μm, 600μm, 766μm, 1180μm and 1760μm. Five samples of each particle sizes for volume fraction of 10%, 20%, 30%, 40% and 50% of the samples were subjected to mechanical test which include; tensile, flexural, hardness, and impact test.

They concluded that decrease in particle sizes increases the tensile strength and flexural strength, but causes a scattered diagram in hardness strength and the impact test. The strength increases with increase in particle size, the tensile and the flexural strength rises highest at 30% content where it then decreases sharply, but in hardness and impact test, increase in filler content increases the BHN and impact strength.

Davallo*etal*., (2010), also studied the mechanical behavior of unsaturated polyester resin used for the composite materials and determined various important parameters, such as tensile, single edge-notch tensile fracture toughness, flexural properties and fracture energy. Periwinkle shells

which are calcium carbonate-filled organic matrix shells are impervious to water and this property makes it possible for periwinkle shells and their derivatives to have very wide applications.

Aku*et al.*, (2010), conducted an XRF analysis on PWS and confirmed that SiO_2, CaO, MgO, Cr_2O_3, and Fe_2O_3 were found to be major constituents of the periwinkle ash. Silicon dioxide, iron oxide, Cr_2O_3 and CaO are known to be among the hardest substances.Some other oxides like K_2O, Na_2O, and MnO were also found to be present in traces. The presence of hard elements like SiO_2, CaO, Cr_2O_3, and Fe_2O_3 suggested that, the periwinkle shell particles can be used as reinforcing material.

Ofem and Umar (2012), studied the effect of filler content on the mechanical properties of periwinkle shell reinforced cashew nut shell liquid resin composites with particle sizes (400, 600, 800μm) and filler loading (10, 20, 30, and 40%) and reported that 30% Filler content gave the best properties, while the highest tensile and flexural strengths were recorded at 30% filler content and 400 μm particle sizes.The highest tensile modulus and impact strength were recorded at 800 μm particle sizes but 30% and 40% filler content respectively. At 40% filler content the properties tends to decrease, indicating that the optimum properties can be achieved at 30% filler content.

Nwanonenyi *et al*., (2013), carried out the effects of particle sizes, filler contents and compatibilization on the properties of linear low-density polyethylene filled periwinkle shell powder practically showed that preparation of thermoplastic composite using linear low density and periwinkle shell powder is possible. The tensile strength, tensile modulus, flexural strength, impact strength, hardness, and specific gravity of the linear low density polyethylene composite

were found to increase with increase in filler and compatibilizer contents respectively, and decrease in filler particle size.

Ofem *et al*., (2013), also investigated the mechanical properties of the hybrid composite made of periwinkle shells (PWS) and rice husk as reinforcing fillers using cashew nut shell liquid resin composite as the matrix. With PWS particle sizes (400, 600, 800μm) and filler loading(10, 20, 30%), the results shows that the highest tensile and flexural strengths were obtained at 30% filler content and 400μm particle sizes. The highest tensile modulus and impact strength were obtained at 800μm and 400μm particle sizes, respectively, for the same percentage of filler content.

Njoku *et al.,* (2011), studied the effects of variation of particle size and weight fraction on the tensile strength and modulus of Periwinkle reinforced composite and reported that, periwinkle particle size within the range of particle sizes (400 - 1000μm) studied has negligible effect on the Young's modulus of Periwinkle reinforced composite.

The tensile strength of Periwinkle reinforced composite increases with decreasing particle size and both tensile strength and Young's modulus of the composite material increase with increasing weight fraction of periwinkle particles in the composite laminate.

Olufemi and Joel (2009), studied the suitability of periwinkle shells, a small gastropod sea snail (mollusk), as a replacement of river gravel in concrete production. Concrete cubes were prepared using proportions of 1:0, 1:1, 1:3, 3:1 and 0:1 periwinkle shells to river gravel by weight, as coarse aggregate and the bulk density of the periwinkle shells was found to be 515 kg/m^3 while that for river gravel was 1611 kg/m^3.

The aggregate impact values for periwinkle shells and river gravel were 58.59 % and 27.1 % respectively and density, workability and the compressive strength of periwinkle concrete increased with increasing inclusion of river gravel. They concluded that periwinkle shells can be

used as partial replacement for river gravel in normal construction works especially in places where river gravel is in short supply and periwinkle shells are readily available.

Tanaka *et al.,* (2004), carried out study on polymer nanocomposite as dielectric and electrical insulation perspectives for processing technologies, material characterization and future application. He investigated that polymer nanocomposite comprise of a polymer or copolymer having nanoparticles or nanofiller scattered in the polymer grid. The nanofiller has significant effect on the physical, compound, mechanical and electrical properties of polymer, such change is frequently good to engineer reason.

Mirjalili *etal.,* (2014), investigated the synthesis of nanoparticles and preparation and characterization of nanopolymer matrix composites. He found that, nano α-alumina particles were synthesized by a sol-gel method using aqueous solutions of aluminum isopropoxide and 0.5M aluminum nitrate. He concluded that, the higher convergence of nano α-Al_2O_3 stacking brought about decrease of those mechanical properties, which could because of agglomeration of nano α-Al_2O_3 particles.

Mayes and Lara (2006), carried out study on high voltage properties of insulating material measured in the ultra wideband. They found that, numerous dielectrics have been developed for various high-voltage high-power microwave applications. They concluded that, development of an insulation processing and testing system for engineering and verifying solid and resin/epoxy dielectric insulators for high-voltage radar systems in the pulse regime. The system tests material properties at high voltages over a frequency range of 100 MHz to 10 GHz.

Joshi and Grewal (2012), carried out some work on synthesis and dielectric behavior of nano-scale barium titanate. They reported that, synthesis of nano-scale barium titanate powder by sol-gel and hydrothermal methods and characterization of the synthesized Barium Titanate

wasconducted by using X-ray diffraction for crystallite size, Transmission Electron Microscopy for particle size and the scanning electron microscopy for surface morphology. They concluded that,the synthesis through hydrothermal process produced a material with higher dielectric constant of 4000compared to the Sol-gel route value of 1600.The dissipation factor was found to be below 0.3 over a wide range of frequencies for powders generated using both processes.

2.2 DIELECTRIC THEORY

Dielectric materials or dielectric are the material in which the electrical conduction is prevented from occurring. These materials are known as *INSULATORS* when they are used to prevent the flow of electricity through them on the application of potential difference, but when they are used to store electrostatic charges and release the same under controlled conditions, they are known as *DIELECTRIC* (Daintith *et al.*,1994).

2.2.1 ELECTRIC SUSCEPTIBILITY AND ELECTRICAL CONSTANT

The electric susceptibility χ_e of a dielectric material is a measure of how easily it polarizes in response to an electric field. This determines the electric permittivity of the material and thus influences many other phenomena in that medium, from the capacitors to the speed of light. It is defined as the constant of proportionality relating an electric field E, to the induced dielectric polarization density P, such that (Daintith *et al.*,1994).

$$P = \varepsilon_o \chi_e \mathrm{E} \quad (2.1)$$

where ε_o is the electric permittivity of free space, the susceptibility of a medium is related to its relative permittivity or dielectric constant, ε_r by

$$\chi_e = \mathrm{\varepsilon}_r - 1 \quad (2.2)$$

So, in the case of a vacuum, $\chi_e = 0$

The electric displacement D is related to the polarization density P by

$$D = \varepsilon_o E + P = \mathfrak{E}_0(1 + \chi_e)E = \mathfrak{E}_r \mathfrak{E}_0 E \text{ (2.3)}$$

The shape of the susceptibility with respect to frequency characterizes the dispersion properties of the material (Daintith *et al.*,1994).

2.2.2 DIELECTRIC POLARIZATION

Dielectrics are materials that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric field that reduces the overall field within the dielectric itself.

If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axes align to the field. The study of dielectric properties concerns storage and dissipation of electric and magnetic energy in materials. Understanding the dielectrics properties of certain material is important in explaining various phenomena in electrical, electronics, optical and solid-state devices (Daintith *et al.*,1994). The process of producing electric dipoles by an electric field is called polarization in dielectrics. Polarization P is defined as the dipole moment per unit volume averaged over the volume of a cell.

$$P = \frac{V}{d} \text{(2.4)}$$

where v is volume of the cell and d is dipole moment.

When a dielectric material is placed in an electric field, the displacement of electric charge gives rise to the creation of dipole in the material. The polarization P of an elementary particle is directly proportional to the electric field strength E.

$$P \propto E (2.5)$$

$$P = \alpha E \ (2.6)$$

where α = polarizability constant

There are many types of polarization such as Electronic, Ionic, Orientation and Space charge polarization

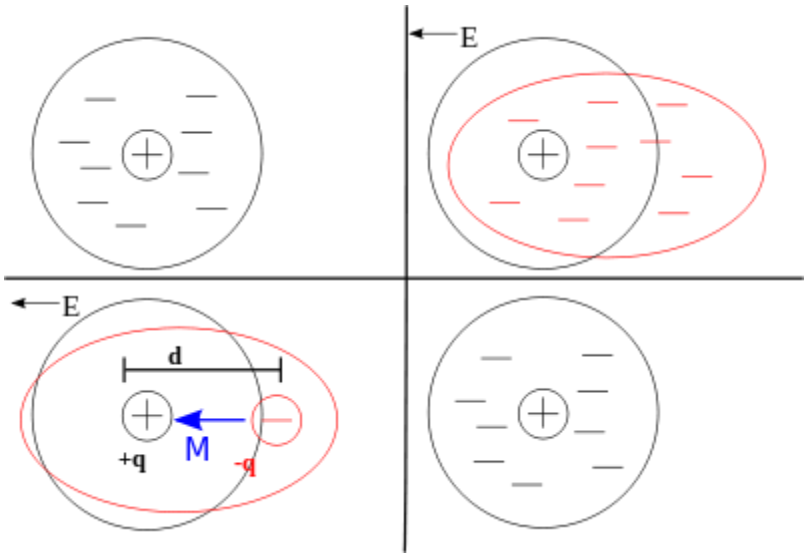


Figure 2.1. Show an electric field in positive and negative point charges.

In the classical approach to the dielectric model, a material is made up of atoms. Each atom consists of a cloud of negative charge (electrons) bound to and surrounding a positive point charge at its center. In the presence of an electric field, the charge cloud is distorted. A dipole is characterized by its dipole moment, it is the relationship between the electric field and the dipole moment that gives rise to the behavior of the dielectric (Arthur *et al.*, 1954).

The relationship between the electric field, **E** and the dipole moment **M** gives rise to the behavior of the dielectric, which, for a given material, can be characterized by the function **F** defined by the equation:

$$M = F(E) (2.7)$$

2.3 FREQUENCY DEPENDENCE OF PERMITTIVITY

The frequency dependence of the susceptibility leads to frequency dependence of permittivity, the shape of the susceptibility with respect to frequency characterizes the dispersionproperties of the material.A dielectric permittivity spectrum over a wide range of frequencies, ε′ and ε″ denote the real and the imaginary part of the permittivity.

$$\varepsilon' = \frac{C}{C_0} \quad (2.8)$$

where C is capacitance, C_0 is free space capacitance and ε' is real part of the permittivity

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2.9)$$

where tan δ is dissipation or loss angle and ε'' is imaginary part of the permittivity.

The ionic dipolar relaxation, atomic and electronic resonances at higher energies, as opposed to the response of a vacuum, the response of normal materials to external fields generally depends on the frequency of the field. This frequency dependence reflects the fact that a material's polarization does not respond instantaneously to an applied field.

The response must always be *causal* which can be represented by a phase difference. Permittivity is often treated as a complex function of the (angular) frequencyω of the applied field,the response of a medium to static electric fields is described by the low-frequency limit of permittivity, also called the static permittivity.

$$\varepsilon \rightarrow \ddot{\varepsilon}(\omega) \quad (2.10)$$

$$\varepsilon = \lim_{\omega \to 0} \ddot{\varepsilon}(\omega) \quad (2.11)$$

$$\ddot{\varepsilon} = \frac{D_o}{E_o} = |\varepsilon| e^{i\delta} \quad (2.12)$$

where ω is angular frequency, Ɛ is electric permittivity; D_o is electric displacement and E_o is electric field of free space.

However, in the narrow frequency ranges that are often studied in practice, the permittivity can be approximated as frequency-independent or by model functions. Dielectric relaxation is the momentary delay or lag in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium. Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (for inductors or transformers).

This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation (Debye *et al., 1913*).

2.3.1 DEBYE RELAXATION

Debye relaxation is the dielectric relaxation response of an ideal, non-interacting population of dipoles to an alternating external electric field. It is usually expressed in the complex permittivity ε of a medium as a function of the field's frequencyω:

$$\hat{\varepsilon}_{(\omega)} = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1+i\omega\tau} \quad (2.13)$$

where ε_{∞} is the permittivity at the high frequency limit, $\Delta\varepsilon = \varepsilon_s - \varepsilon_{\infty}$where $\varepsilon_s$is the static, low frequency permittivity, and τ is the characteristic relaxation time of the medium (Debye *et al.*, 1913).

2.3.2 CAPACITORS

A capacitor is a passive two terminal electrical component that stores electrical energy in an electric field. The effect of a capacitor is known as capacitance and dielectric reduces the field and increases the capacitance, the uses of a solid dielectric material with high permittivity as the intervening medium between the stored positive and negative charges.

This material is referred to in technical contexts as the capacitor dielectric.This can be seen by treating the case of a linear dielectric with permittivity ε and thickness d between two conducting plates with uniform charge density σ_ε. In this case the charge density is given by

$$\sigma_\varepsilon = \varepsilon \frac{V}{d} \quad (2.14)$$

and the capacitance per unit area by

$$C = \frac{\sigma_\varepsilon}{V} = \frac{\varepsilon A}{d} \quad (2.15)$$

From this, it can easily be seen that a larger ε leads to greater charge stored, greater capacitance and A is the cross-section area (Arthur *et al.*, 1954).

2.4 HIGH VOLTAGE INSULATION

An electrical insulator is a material whose internal electric charges do not flow freely, and therefore make it nearly impossible to conduct an electric current under the influence of an electric field. The property that distinguishes an insulator is its resistivity; insulators have higher resistivity than semiconductors or conductors.

Investigations show that, a perfect insulator does not exist, because even insulators contain small numbers of mobile charges (charge carriers) which can carry current, insulators become electrically conductive when a sufficiently large voltage is applied that the electric field tears electrons away from the atoms, this is known as the breakdown voltage of an insulator. It was found that, insulators are used in electrical equipment to support and separate electrical conductors without allowing current through themselves. An insulating material used in bulk to wrap electrical cables or other equipment is called insulation (Frank *et al.*, 1921).

Insulators used for high-voltage power transmission are made from glass, or composite polymer materials. Investigation shows that, electric utilities have begun converting to polymer

compositematerials for some types of insulators. Composite insulators are less costly, lighter in weight, and have excellent hydrophobic capability (Holtzhausen *et al.*, 2001)

2.4.1CONDUCTION IN SOLIDS

Electrical insulation is the absence of electrical conduction, electronic band theory says that a charge flows if states are available into which electrons can be excited. Report show that, allows electrons to gain energy and thereby move through a conductor such as a metal, insulators have a large band gap, this occurs because the "valence" band containing the highest energy electrons is full, and a large energy gap separates this band from the next band above it.

Investigation show materials that lack electron conduction are insulators if they lack other mobile charges as well.An electrolytes and plasmas contain ions and act as conductors whether or not electron flow is involved (Diesenderf *et al.*, 1974).

2.4.2 THERMAL CONDUCTIVITY

Thermal conductivity (denoted k, λ, or κ) is the property of a material to conduct heat. It is evaluated primarily in terms of Fourier's Law for heat conduction. Heat transfer occurs at a lower rate across materials of low thermal conductivity than across materials of high thermal conductivity. Materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. The thermal conductivity of a material may depend on temperature. The reciprocal of thermal conductivity is called thermal resistivity (*Perry and Green, 1997).*

The heat flowing into the sample is given by.

$$H_{in} = VI \tag{2.16}$$

where V is voltage and I is current flow through the sample

The heat flowing out of the hot end is given by.

$$H_{out} = KA\frac{\theta_2 - \theta_1}{L} \quad (2.17)$$

where A is the cross-sectional area and L is the diameter of the sample.

In equilibrium, the heat in equals the heat out

$$VI = KA\frac{(\theta_2 - \theta_1)}{L} \quad (2.18)$$

$$K = \frac{VIL}{A(\theta_2 - \theta_1)} \quad (2.19)$$

The cross-sectional area $A = \frac{1}{4}\pi d^2$ then, the thermal conductivity K, become

$$K = \frac{VIL}{\frac{1}{4}\pi d^2(\theta_2 - \theta_1)} \quad (2.20)$$

The units of Kare $Wm^{-1}K^{-1}$

2.4.3 BREAKDOWN **AND HIGH VOLTAGE**

When subjected to a high enough voltage, insulators suffer from the phenomenon of electrical breakdown. It was reported that, when the electric field applied across an insulating substance exceeds in any location the threshold breakdown field for that substance, the insulator suddenly becomes a conductor, causing a large increase in current, an electric arc through enough to accelerate free charge carriers to a high enough velocity to knock electrons from atoms when they strike them, ionizing the atoms.

Bakshi *et al.*,(2007), reported that, freed electrons and ions are in turn accelerated and strike other atoms, creating more charge carriers, in a chain reaction. In a solid, the breakdown voltage is proportional to the band gap energy (Bakshi *et al.,* 2007).In electronic devices; the tiny and delicate active components are embedded within nonconductive epoxy or phenolic plastics, or within baked glass or ceramic.

Diesenderf*et al.*,(1974), reported that, in high voltage systems containing transformers and capacitors, liquid insulator oil is the typical method used for preventing arcs. The oil replaces air in spaces that must support significant voltage without electrical breakdown.High voltage system insulation materials include ceramic or glass wire holders, gas, vacuum, and simply placing wires far enough apart to use air as insulation.

The conductors for high-voltage electric power transmission are bare, and are insulated by the surrounding air. It was also found that, Conductors for lower voltages in distribution may have some insulation but are often bare as well. Insulators are also required where the wire enters buildings or electrical devices, such as transformers or circuit breakers, to insulate the wire from the case. These hollow insulators with a conductor inside them are called bushings (Diesenderf *et al.*, 1974).

CHAPTER THREE

MATERIALS AND METHODS

3.0 MATERIALS AND EQUIPMENT

This chapterpresents the materials, equipments and methodology used during the course of research work.

3.0.1 MATERIALS

The materials used in this research include: periwinkle shells, epoxy resin and hardener, silicone oil, liquid binder, water, cotton wool and sieve, beaker, conical flask, measuring cylinder.

3.0.2 EQUIPMENT

The equipment used include; Crusher machine, Ball milling machine, Digital weighing balance, Magnetic stirrer, Programmable LCR Bridge, Scanning Electron Microscope (SEM), X-ray fluorescence (XRF), Searle's thermal conductivity apparatus, Monsanto Tensometer, Universal material testing machine, Vickers hardness tester and Charpy Impact testing machine.

3.1 METHOD

This section present Sample preparation, characterization of Morphology, elemental composition, thermal conductivity,mechanical and dielectric properties of polymer composite.

3.1.1 SAMPLE PREPARATION

This section present sample preparations of periwinkle shell powder, Preparation of polymeric composite and Molding of the polymer composite materials.

3.1.1.1 SAMPLE PREPARATION OF PERIWINKLE SHELL POWDER

The periwinkle shells were properly washed with water followed by acetone. They were then dried in an oven at 100 ºC for 48 hours to completely remove moisture from it. The cleaned periwinkle shells were passed through a turning operation on a crusher and ball milling machine

to produce powder. This was done at the Department of Chemical Engineering, Ahmadu Bello University Zaria, Nigeria. The crushed particles were sieved using a 0.15mm sieve produced from the shell to become fine powder.

3.1.1.2 PREPARATION OF POLYMERIC COMPOSITE

The polymer was prepared by ratio 3:1 (48 ml and 16 ml) of epoxy resin to hardener by weight as specified by the manufacturer (Gougeon Brothers Inc, Bay City USA). The polymer composite was produced by stir casting method (is a type of casting process in which a mechanical stirrer is introduced to form vortex to mix reinforcement in the matrix material). About 58 g and 15 g (total 73 g) of epoxy and hardener were measured in two separate beakers using weighing balance. The measured epoxy and hardener were separately degassed in a vacuum oven for 8 minutes at a temperature 40^{o}C to remove the air bubbles from the solutions. Each of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1% of periwinkle shell powder was mixed with hardener properly using magnetic stirrer. The two solutions were mixed in a beaker at about 40ºC. This temperature was maintained and the solution was mixed and stirred thoroughly with a magnetic stirrer for 15 minutes. This was followed by a second degassing for 5 minutes under vacuum in the oven at the temperature 40^{o}C and it was removed from the oven for moulding.

3.1.1.3 MOULDING OF THE POLYMER COMPOSITE MATERIALS

The hand lay-up method of fabrication was applied. Silicone oil release agent was applied to the surface of mould (the dimension of the mould is 17mmx18mm× 2mm) for easy removal of the samples and then the samples were transfered to the mould by pouring it on the surface.



PlateII. Mould with sample

The mixture was left for 48 hours to cure on the mould. Seven samples were produced and the individual samples were removed from the mould. The freehand cutting was used to cut the samples produced into different shapes for electrical and mechanical measurement to take the average values of the samples, and identification numbers were inscribed on them.

Table 3.1. Sample identification numbers of compositions and their percentages

Sample A (circular shape)	Sample B (dumbbell shapes)	Sample C (cubic shape)	Percentage (%) of periwinkle shell powder
A1	B1	C1	0.0
A2	B2	C2	0.5
A3	B3	C3	0.6
A4	B4	C4	0.7
A5	B5	C5	0.8
A6	B6	C6	0.9
A7	B7	C7	1.0

The last step was post-curing of the samples in vacuum oven for one hour at a temperature of 100ºC followed by a slow cooling overnight to room temperature and ensured that, the dispersed powder in Epoxy resin is completely cured. PlateII – V show the samples produced.

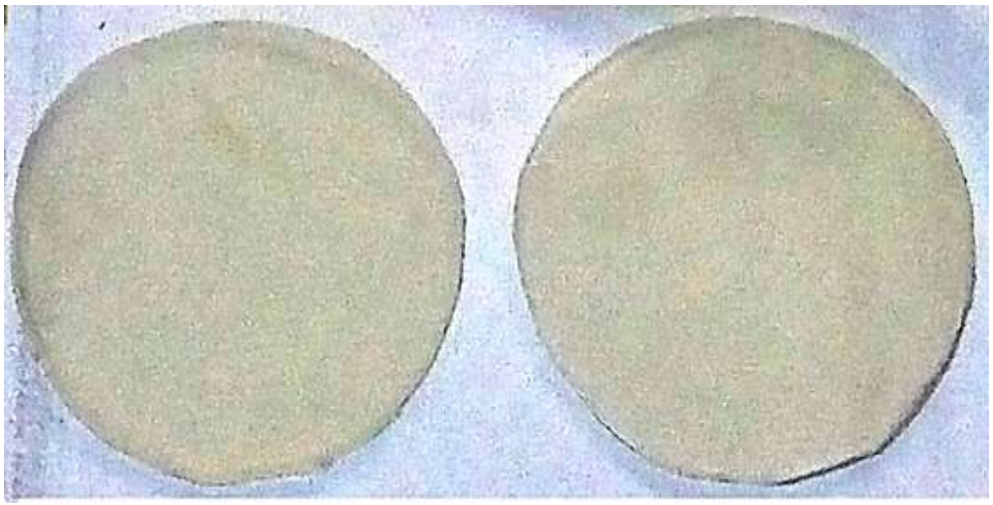


Plate III.Sample A with different percentage of the powder forhardness and dielectric properties test



Plate IV. Sample B with different percentage of the powder for tensile strength



PlateV. Sample C with different percentage of the powder for compressive and impact strength test

3.1.2 CHARACTERIZATION

Some parameter has been characterized such as Elemental composition, Morphology analysis,Thermal conductivity, Tensile strength test, Compressive strength test, Hardness test, Impact test, Real and Imaginary permittivity, Resistivity and Electrical Conductivity.

3.1.2.1 ELEMENTAL COMPOSITION

The elemental composition of the Periwinkle shells powder was determined using X-ray Fluorescence (XRF) machine (Oxford instrument, X-supreme 8000). The powder obtained from periwinkle shell was loaded in the sample chamber of the spectrometer and the machinewas operated at an accelerating voltage of 30 V and current of 10 mA to produce the X-rays to excite the sample for 10 min.

The Fluorescent X-rays emitted by the material sample are directed into a solid-state detector which produces a continuous distribution of pulses, the voltages of which are proportional to the incoming photon energies and the diffraction grating used is usually a single crystal, the angle of

incidence and take-off on the crystal, a single X-ray wavelength was selected. The counter is a chamber containing a gas that is ionized by X-ray photons and the signal is amplified, transformed into an accumulating digital count. The system is controlled by a PC running the dedicated Mini Pal analytical software.

3.1.2.2 MORPHOLOGY ANALYSIS

The microstructure of the samples was studied using a Scanning Electron Microscope(SU1510, CompactHitachi High-Technologies,SEM) equipped with an energy dispersive spectroscopy system. This was done at the Electrical Engineering Department, Kwara State University, Malate, Kwara State, Nigeria. The samples were held on the sample holder using a double-sided carbon tape before putting them inside the sample chamber and SEM was operated at an accelerating voltage of 16 kV and the image was recorded.

3.1.3 THERMAL PROPERTIES

The thermal conductivity of the periwinkle shell powder and the pelletized powder was measured using Searle's apparatus.

3.1.3.1 THERMAL CONDUCTIVITY

A pellet of diameter 40 mm and thickness 2 mm was prepared from the periwinkle shell powder.Liquid binder (methyl cellulose) was added to the periwinkle shell powder (to pelletize the powder); it was carefully mixed and pressed into a pellet using a hydraulic press in a die by applying four tones load for 120s.



Plate VI. A pelletized periwinkle shell powder using a hydraulic press

The Searle's method was used to determinethe thermal conductivity of pelletized powder of the solids. The pelletized sample was placed in the sample chamber and heated at one end by means of an electrical power supply.Water was made to flow through the apparatus, entering the tube at the end of the steam chamber and leaving at the near to it. When water was flowing, power supply was switched on, and the input current and voltage were recorded.Water starts to get hotter until a constant temperature difference is reached and its flow was adjusted so that the temperature difference is about 5ºC. Thermometers θ_1 and θ_2 were placedwhere water come in and went out to measure the temperatures of the outgoing and incoming water. The temperatures $\theta_1$and θ_2 were recorded from the thermometers after they attained constant values. The experiment was repeated three times to have average value for thermal conductivity of the pelletized powder sample. The maximum values of voltage, current and temperatures were recorded and it was used to calculate the thermal conductivity, K of the pelletized periwinkle shell powder using equations 2.19 and 2.20

Figure 3.1 shows the setup of searle's apparatus to determined the thermal conductivity of the pelletized periwinkle shell powder.

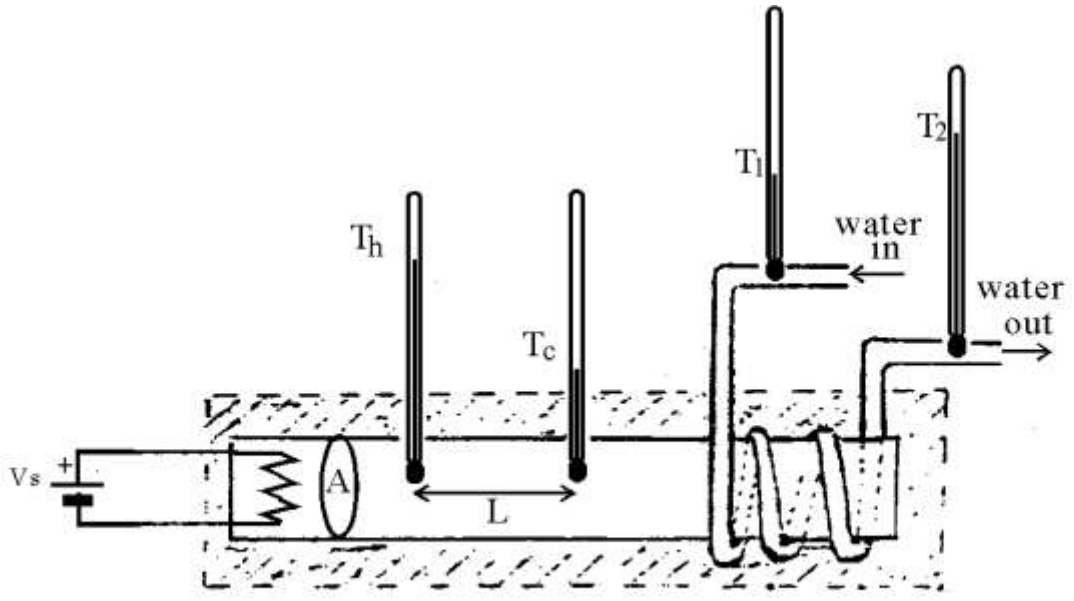


Figure 3.1.Searle's experimental setup for measuring the thermal conductivity of the pelletized periwinkle shell powder.(*Perry and Green, 1997).*

3.1.4 MECHANICAL PROPERTIES

The mechanical properties of the produced composite polymeric samples were determined. These properties included; tensile strength, compressive strength, hardness and impact strength.

3.1.4.1 TENSILE STRENGTH TEST

The samples B was cut into dumb bell shape and Monsanto Tensometer was used to perform the tensile test. The tensile test samples were machined to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E8. The samples were fixed and held by the gauge at both ends of the testing apparatus. The maximum loads were recorded from the Monsanto tensometer. The load was then applied until the samples failed (fracture).The two broken ends of the samples were fitted together and final gauge length was measured. The readings obtained were used in the calculation of the sample tensile strength in MPa with the relation:

$$Tensile\ strengths = \frac{Force\ (F)}{Area\ (A)} \quad (3.1)$$

3.1.4.2 COMPRESSIVE STRENGTH TEST

The compression test samples C were machined to standard dimensions prior to operation. The test was performed using the Universal material testing machine. The tensile test samples were machined to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E8. Five sets of sample C were used for the determination of compressive strength and it was placed on the disc sample chamber which was connected to the meter for reading the maximum load. Then pressure was applied to the apparatus to compress the sample placed on the disc sample chamber. The degree of deterioration was evaluated by measuring the reduction in compressive strength by the expression: The maximum load was recorded and it was used to calculate the compressive strength with the relation:

$$Compressive\ strengths = \frac{force\ /maximum\ \ load\ \ (F/L)}{cross-section\ \ area\ \ (A)} \quad (3.2)$$

3.1.4.3 HARDNESS TEST

The hardness tests of the samples A were performed with standard dimensions. The hardness values were determined using Vickers hardness tester. The hardness test samples were prepared to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E18. The samples A were prepared with flat surfaces, which act as a support for the test samples and a load of 0.1 N was applied to the samples in a controlled manner without inducing impact or vibration, which was maintained for 10 minutes. The diagonals of the impression were measured and the reading was taken when the large pointer came to rest.

3.1.4.4 IMPACT TEST

The impact test samples were machined to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E23. The test gives an idea of the energy required to break a

notched sample under standard conditions. The test was performed using Charpy impact testing machine (capacity 15 J) with a Charpy sample of 10 mm diameter and 100 mm length with a 2 mm deep notch. The test sample was then placed in the chamber of the Charpy impact testing machine. The trigger was released and the registering pointer of the quadrant scale indicated the energy absorbed in Joules to break the sample. The energy absorbed in breaking the sample was recorded and the same was repeated for other test samples.

3.1.5 ELECTRICAL PROPERTIES

The pellets of periwinkle shell powder were compacted at different temperatures to study the effect of compacting parameter on dielectric properties. The pelletized powder was inserted into two electrode test cell which was placed in the temperature controlled chamber to vary the temperature of the samples. Dielectric measurements were taken at room temperature, 40, 50, 60, 70 and 80ºC. The samples were inserted into sample holder (two electrode test cell) and terminal of the test cell were connected to programmable LCR Bridge of frequencies range 200 Hz to 50 kHz.The capacitance, resistance and dissipation of the samples were determined within the frequency of 200 Hz and 50 kHz by applying 1 V potential difference across the test capacitor.

3.1.5.1 REAL AND IMAGINARY PARTS OF THE COMPLEX PERMITTIVITY

The real part (ε') and imaginary part (ε'') of the complex permittivity were determined. The real part of the permittivity, is related to the stored energy within the medium while the imaginary part of the permittivity, is related to the dissipation (or loss) of energy within the medium and δ is the loss angle. The maximum values were recorded and it was used to calculate the real and imaginary parts of the complex permittivityusing equations 2.8 and 2.9

3.1.5.2 RESISTIVITY AND ELECTRICAL CONDUCTIVITY

Resistivity and electrical conductivity of the pelletized periwinkle shell powder and polymer composite samples were determined using measured capacitance and resistance. The Resistivity (ρ) is an intrinsic property that quantifies how strongly a given material opposes the flow of electric current and Electrical conductivity (σ) is the reciprocal of electrical resistivity and measures a material ability to conduct an electric current. The maximum values were recorded and it was used to calculate the resistivity and electrical conductivity of the pelletized periwinkle shell powder and polymeric samples using the relations:

$$\rho = R\frac{A}{L} \tag{3.3}$$

where ρ is the Resistivity, R is the electrical resistance; A is the cross-sectional area of the sample and L is the thickness of the sample.

$$\sigma = \frac{1}{\rho} \tag{3.4}$$

where σ is the electrical conductivity measured in Siemens per meter (S/m).

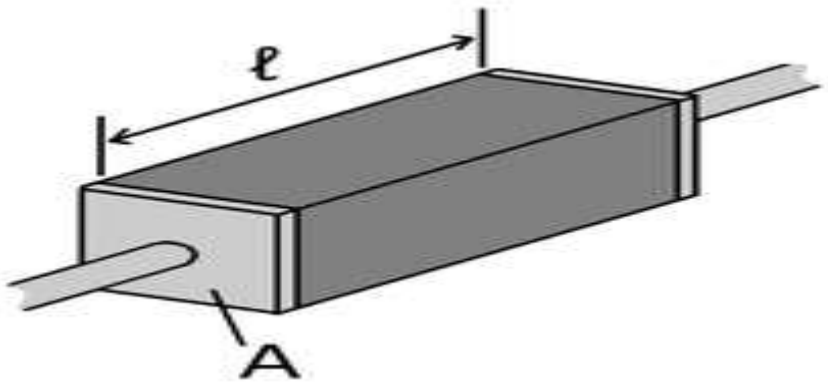


Figure 3.2. A piece of resistive material with electrical contacts on both ends (*Narinder Kumar 2003).*

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

This chapter presents the results and analysis of the test performed. These include; the elemental analysis, thermal properties test, morphology analysis, mechanical properties test and electrical properties test.

4.1ELEMENTAL ANALYSIS OF THE PERIWINKLE SHELL POWDER BY X-RAY FLUORESCENT

Figure 4.1 shows the XRF Spectra of periwinkle shell powder. There appeared two peaks (3.71 and 4.02 keV) on the spectra thatare assigned to calcium. The 3.71 keV peak has the highest intensity, an indication that Calcium is the dominant metal in the sample. Other visible peaks are at 1.71 keV assigned for Silicon, 1.22 keV for Magnesium, 1.42 keV for Aluminum, 6.41 keV for iron and 2.2 keV for Sulfur (Ida and Kawai, 2005) .

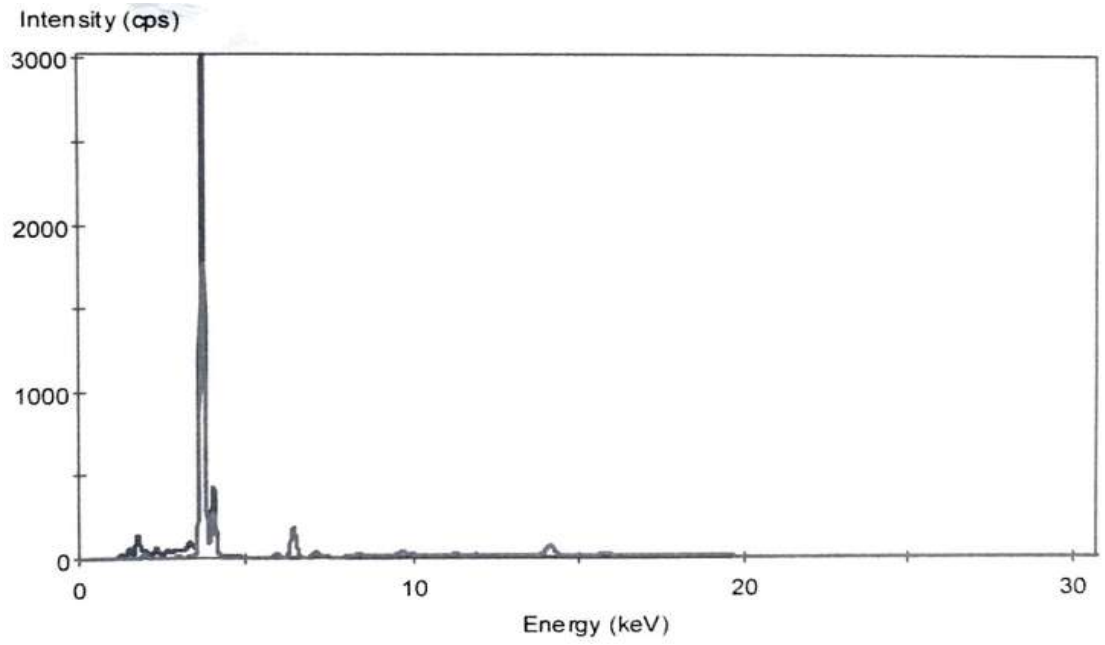


Figure 4.1. XRF Spectra of periwinkle shell powder

The determined chemical composition of the periwinkle shell powder from the spectra analysis as presented in Table 4.1

The shell contained several oxides of metals such as Sodium oxide (Na_2O), Phosphorous oxide (P_2O_5), Titanium oxide (TiO_2), Chromium oxide (Cr_2O_3), Zinc oxide (ZnO), etc with Calcium oxide (CaO) as the dominant metal oxide with concentration of about 81.8%.

Table 4.1. Chemical compositions of periwinkle shell powder as revealed by XRF analysis.

Oxide	**Concentration (wt %)**
Na_2O	0.002
MgO	3.069
Al_2O_3	2.548
SiO_2	6.734
P_2O_5	0.752
SO_3	1.001
Cl	0.280
K_2O	0.295
CaO	81.803
TiO_2	0.147
Cr_2O_3	0.036
Mn_2O_3	0.437
Fe_2O_3	2.380
ZnO	0.010
SrO	0.508

The elemental analysis shows that CaO has the highest compositions in the periwinkle shell powder and it constitutes about 81.8% of the total material composition. SiO_2, MgO, Al_2O_3 and Fe_2O_3 constitute about 15.732% of the material composition. CaO, SiO_2, Fe_2O_3, Al_2O_3, TiO and MgO are among the hardest substances. SO_2, P_2O_3, SrO, Mn_2O_3, K_2O, Cl, Cr_2O_3 and ZnO were also found to be present. The presence of hard compounds such as CaO, SiO_2, Fe_2O_3, Al_2O_3, TiO and MgO confirmed that the periwinkle shell powder can be used as particulate reinforcement in different polymer matrices. The material composition has similarity with XRF analysis of clay which has been used in polymer matrix composite. This reveals the use of periwinkle shell powder as particulate in polymer matrices composite.

4.2 THERMAL CONDUCTIVITY TEST

The thermal conductivity values were calculated to be 16.884553, 20.121950, 16.884553 $Wm^{-1} k^{-1}$, respectively. The average thermal conductivity, *K* of the sample, was calculated to be 17.963685 $Wm^{-1} k^{-1}$. Dielectric materials of good thermal conductive ity are used as electrical insulation as they perform a dual function of insolent and coolant. They are supposed to serve as a medium to transport the heat generated due to ohmic heating in the electrical system. The thermal conductivity values of some of metals oxides are as follows: CuO has a thermal conductivity between 20 and 30 $Wm^{-1} k^{-1}$, SiO_2 is 1.7 $Wm^{-1} k^{-1}$, MgO is 35 $Wm^{-1} k^{-1}$, Al_2O_3 is 35 $Wm^{-1} k^{-1}$, TiO is 9.2 $Wm^{-1} k^{-1}$ and CaO is 15 $Wm^{-1} k^{-1}$ (Nayak and Singh, 2007). Periwinkle shell pellet has a thermal conductivity of 18.0 $Wm^{-1} k^{-1}$ which is close to the thermal conductivity of pure CaO with a thermal conductivity of 15 $Wm^{-1} k^{-1}$. The difference may likely be due to the presence of high thermal conductive metal oxides in the powder. The thermal conductivity is higher than that of TiO_2 and SiO_2. This is an indication that its dispersion in the polymer will produce a composite with better thermal conductive properties

compared with the commonly used TiO_2 and SiO_2. The thermal conductivity of the sample is also slightly higher than that of pure CaO. This is an indication that the sample under study which contained 81.8% CaO is more thermally conducting compared with the pure CaO crystal.

4.3 MICROSTRUCTURAL RESULT

The Scanning Electron Microscopy was used to examine the dispersion of the powder in the polymer. Plate VII-XII show the SEM images of Periwinkle shell powder and epoxy resin composite polymer produce (0.5%, 0.7%, 0.9% and 1%). The size of the powder samples was determined from the images obtained from Scanning Electron Microscopy (SEM) as shown in plate 1. About 4.39 to 100μm size of the powder were produced on scanning the sample and images on the screen were photographed.

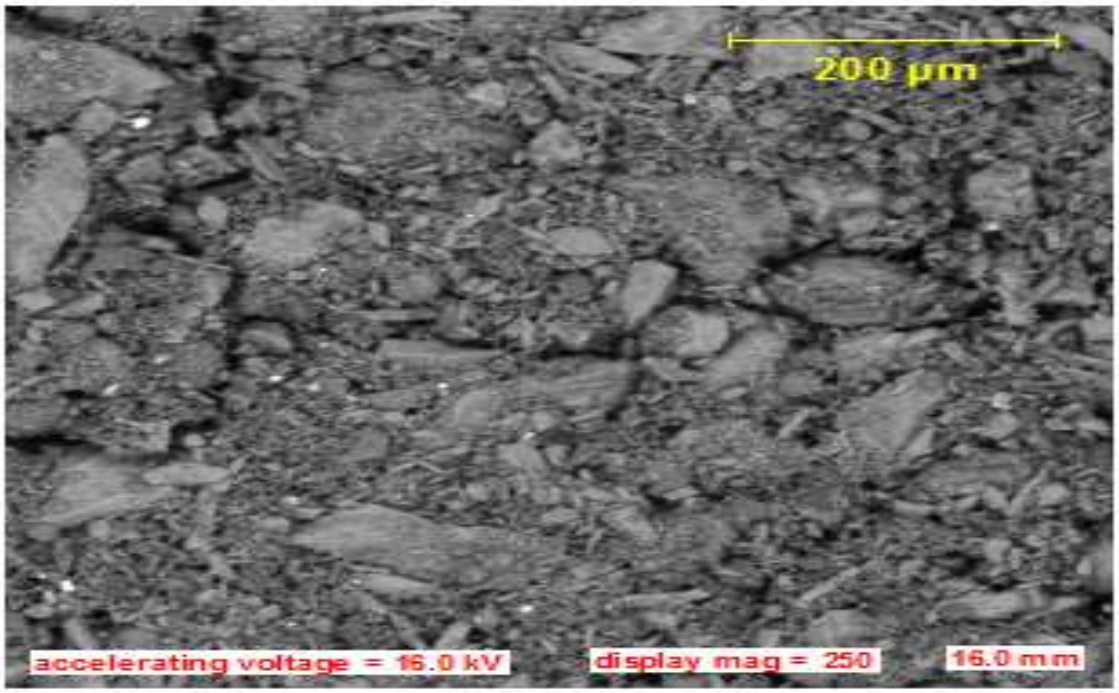


Plate VII. The SEM micrographs of periwinkle shell powder.



Plate VIII.The SEM micrographs of reinforced epoxy resin without periwinkle shell powder.

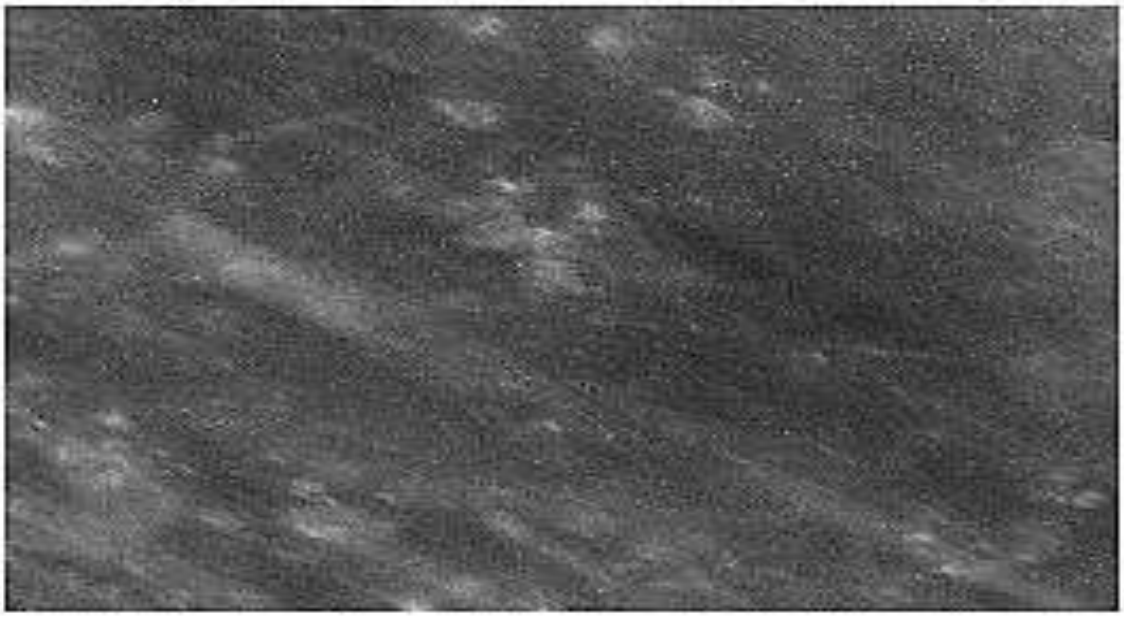


Plate IX. The SEM micrographs of reinforced epoxy resin with 0.5% of periwinkle shell powder.

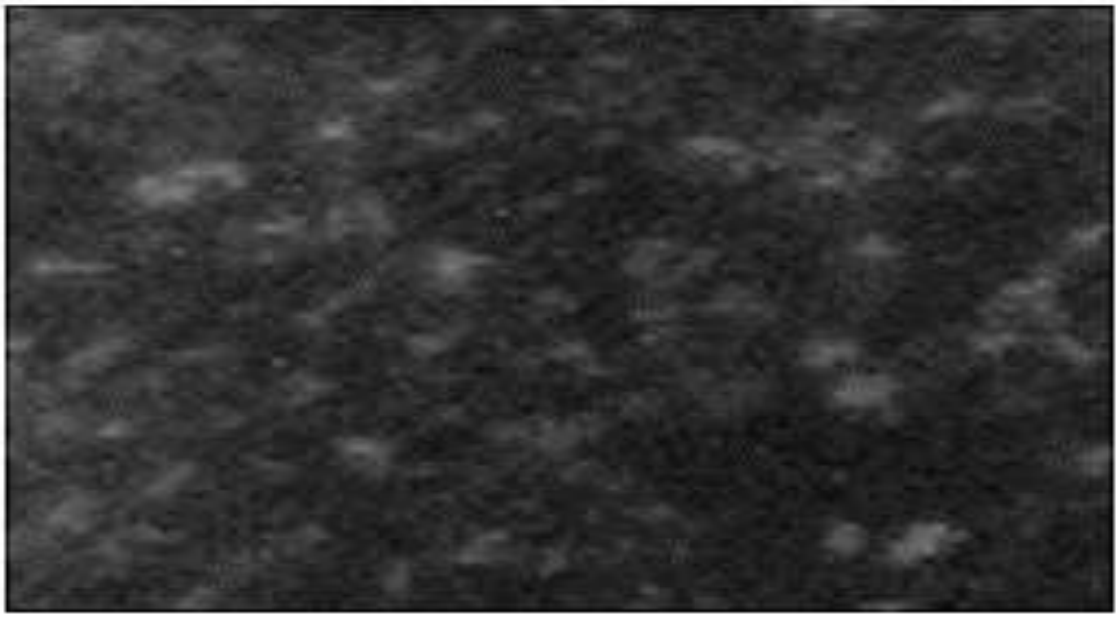


Plate X. The SEM micrographs of reinforced epoxy resin with 0.7% of periwinkle shell powder.



Plate XI. The SEM micrographs of reinforced epoxy resin with 0.9% of periwinkle shell powder.

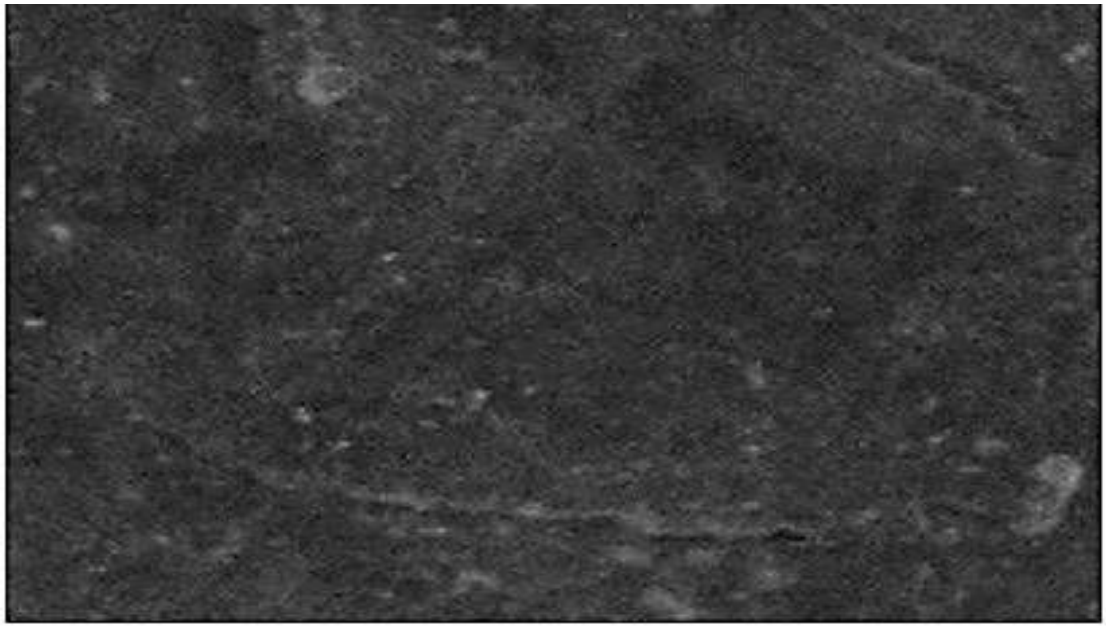


Plate XII. The SEM micrographs of reinforced epoxy resin with 1% of periwinkle shell powder.

The microstructure of the periwinkle shell powder is shown plate 4.1 and the structure contains a network of the θ phase. In plate 4.2, microstructure of neat epoxy polymer shows white region of epoxy resin as polymer reinforcement (strengthen). Plates 4.3-4.6 (0.5, 0.7, 0.9, and 1% of powder), show the microstructure of the epoxy resin reinforced with periwinkle shell powder. The microstructure reveals the distribution of the periwinkle shell powder in the grain boundaries. Plate 4.3 shows the microstructure of reinforced epoxy resin with 0.5% of periwinkle shell powder with structure that indicates dark region of the periwinkle shell powder in white epoxy resin matrix.Plate 4.4, displayed microstructure of reinforced epoxy resin with 0.7% periwinkle shell powder, more dispersed powder particulate in the polymer matrix of reinforced epoxy resin. Plate 4.5, shows microstructure of reinforced epoxy resin with 0.9% of periwinkle shell powder; it is almost like that of plate 4.3 only with more dark region and powder particulate of polymer. The microstructure in plate 4.6 of reinforced epoxy resin with 1% of periwinkle shell powder showed a more randomly distributed periwinkle shell powder in the matrix of epoxy

resin. Therefore, the dark region in the microstructure indicated the presence of the powder fillings while the white region indicates the absence of the powder fillings in the epoxy resin matrix.

4.4 MECHANICAL PROPERTIES

The result obtained from mechanical test of seven polymeric composite samples (tensile strength, compressive strength, hardness and impact strength) are presented in Table 4.2 and Figures 4.2-4.5

Table 4.2 presents the average value of the obtained results from the Tensile, Compressive, Hardness and impact test of the sample only and the samples containing periwinkle shell powder while Figure 4.2 compares the tensile strength of the polymer samples on a bar chart. The chart displayed the influence of the percentage composition of periwinkle shell micro-particle powder in the polymer composites. It is evident that the tensile strength of the polymer increased with the addition of the periwinkle shell micro-powder.

A further increase was also observed in the polymer composite with an increase in the percentage composition of the micro-particle in the polymer. An increase in the tensile strength was observed from polymer only to the samples with the shell microparticle composition of up to 0.9 wt%. A decrease in the tensile strength was observed with the addition of 1 wt% of shell microparticle. It is not certain if 0.9 wt% powder produced a composite with the optimum performance or possible agglomeration was responsible for the lower tensile strength of that sample. Agglomeration may make the material to become brittle and this could result in failure with lesser tension.

Table 4.2. Tensile, compressive, hardness and impact test results

Composition of periwinkle shell powder (%)	Tensile strength (MPa)	Compressive strength (MPa)	Hardness Value (HV)	Impact strength (J)
0.0	31.94	54.31	10.77	5.38
0.5	42.85	76.94	22.28	4.74
0.6	64.05	99.26	27.92	4.48
0.7	76.45	124.68	31.62	3.94
0.8	97.27	135.01	35.48	3.56
0.9	100.94	137.73	37.32	2.68
1.0	77.44	104.78	40.62	1.94

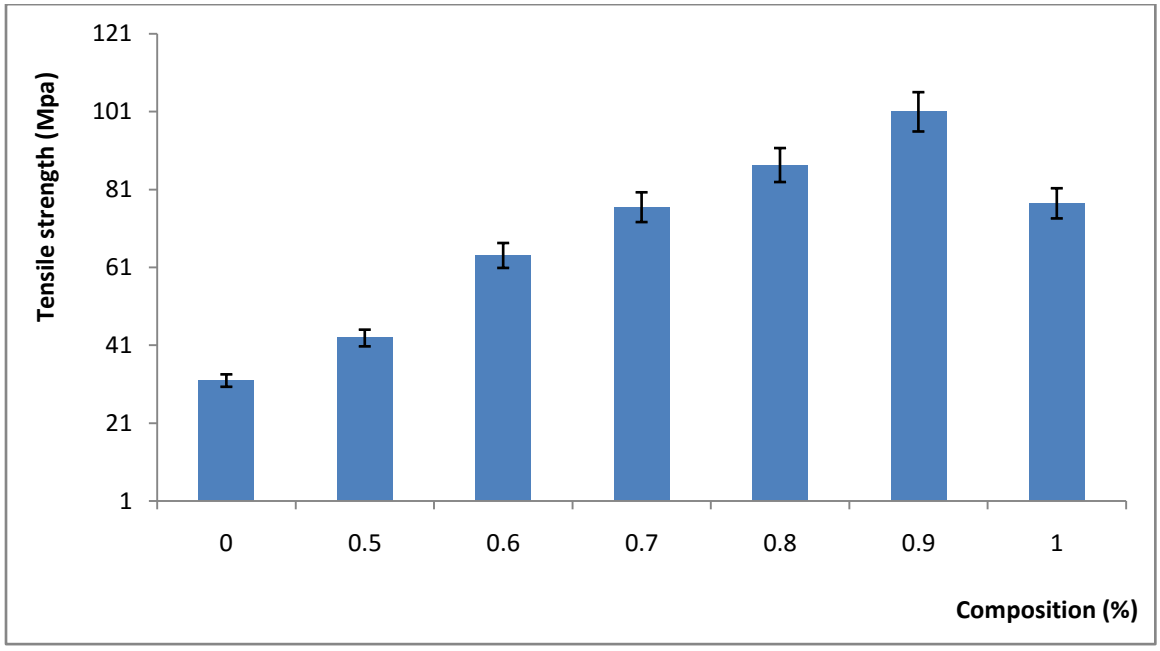


Figure 4.2. Profile of Tensile strength of the samples composition in different percentage powder addition.

The compressive strength test shows a similar result as shown in Figure 4.3. But a steady increase in the compressive strength was obtained up to 0.7%. The further increase shows relative stability of compressive strength to 0.9% concentration. Increasing the content of the powder to 1% shows a decrease in the compressive strength.

The Hardness test result in Figure 4.4 shows a continuous increase as the concentration of the particles increases while the impact value decreases with an increase in the composition of the powder as shown in Figure 4.5. The improved tensile strength recorded from the addition of the periwinkle shell powder results from an increase in the tensile strain of the respective polymer composites. An increase in the quantity of the dispersed powder resulted in an increase in tensile strain. But the dispersion of 0.5wt%powder resulted in a decrease in the tensile strain and a corresponding decrease in tensile strength.

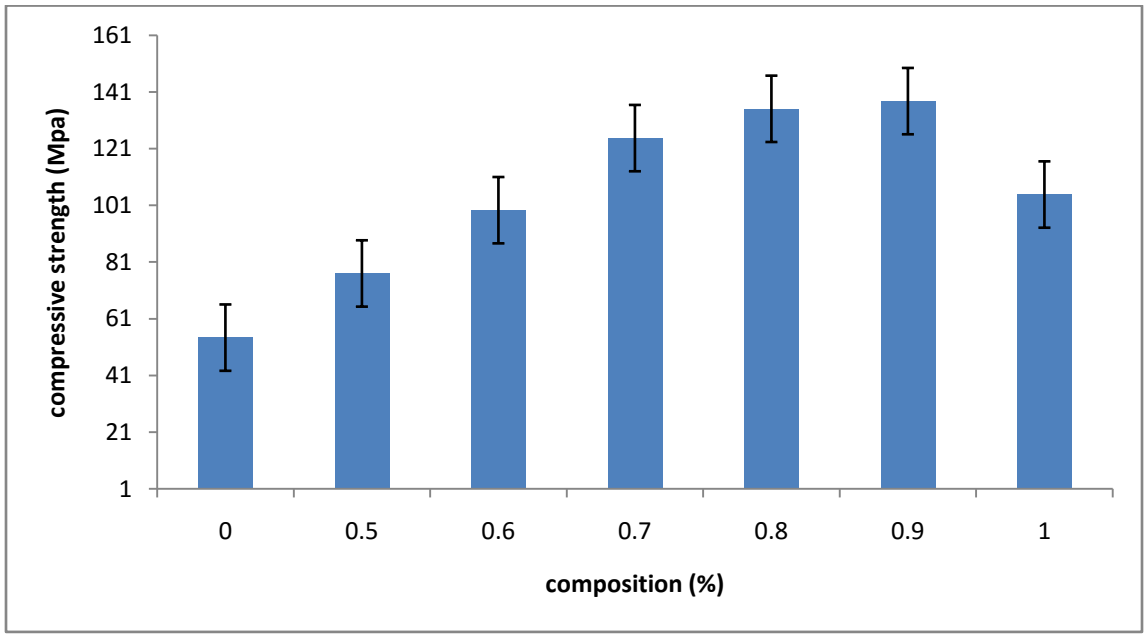


Figure 4.3. Profiles of Compressive strength of the samples composition in different percentage powder addition.

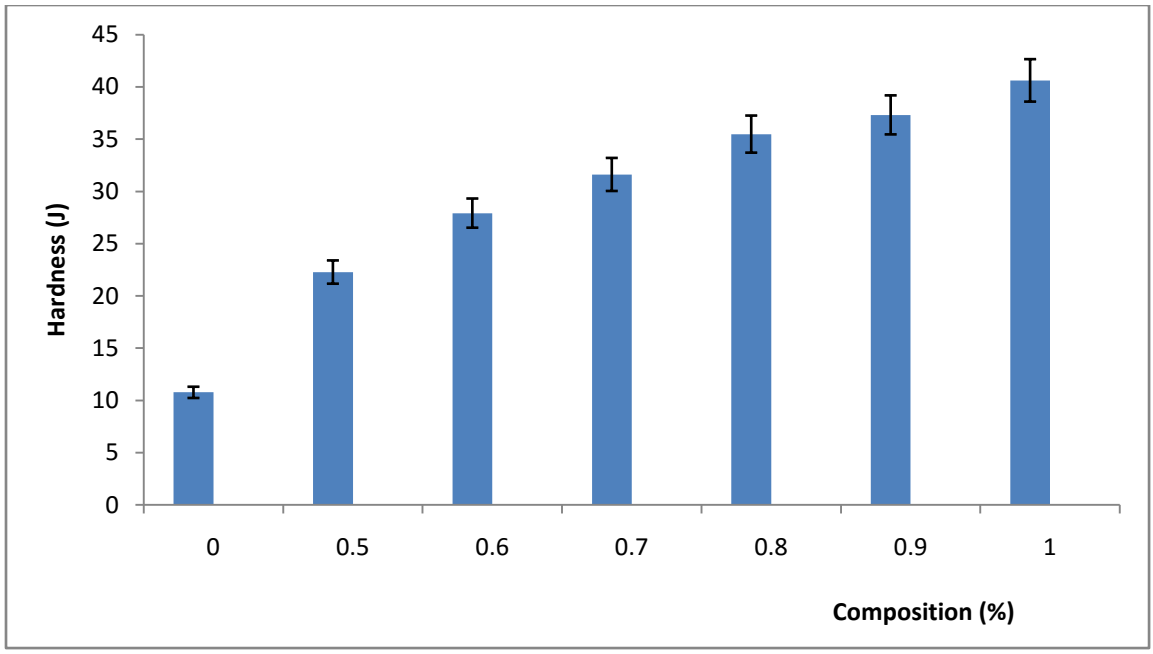


Figure 4.4. Profile of Hardness Value of the samples composition in different percentage powder addition.

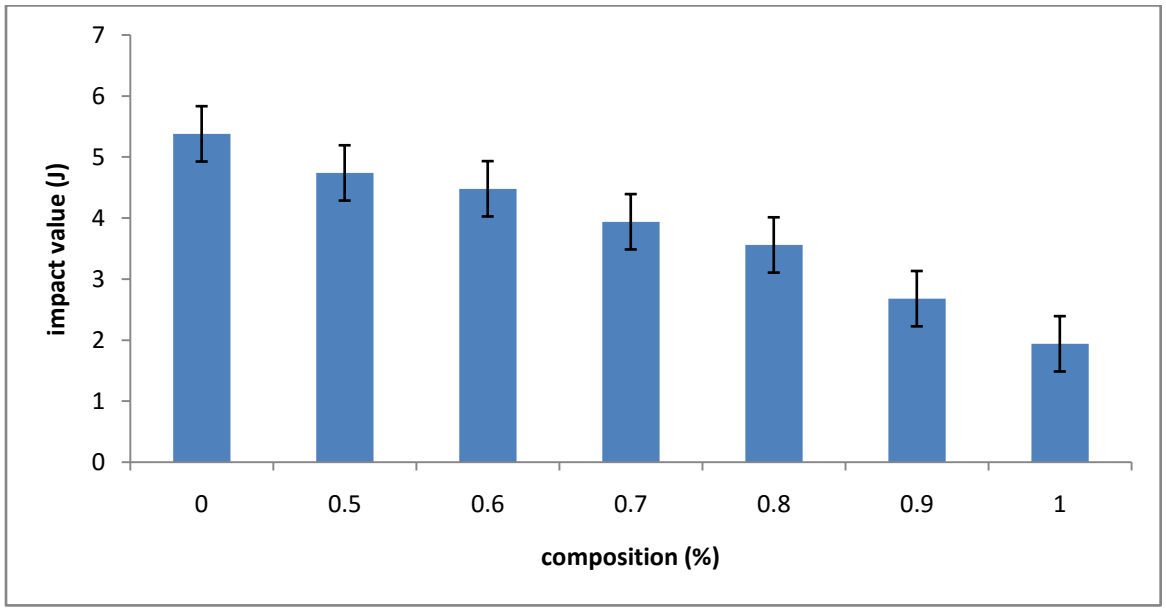


Figure 4.5. Profiles of Impact strength of the sample composition in different percentage powder addition.

The tensile and compressive strength of the samples with different percentage composition as displayed in Figures 4.2 and 4.3 respectively indicate that the tensile and compressive strength increased with increasing percentage of periwinkle shell powder addition to a maximum of 0.9%.

It can be seen from the figures that the samples have highest value of 100.92 and 137.73 MPa for tensile and compressive strength respectively with the addition of 0.9% periwinkle shell powder. These properties decrease to 77.44 and 104.78 MPa for tensile and compressive strength with the addition of 1% periwinkle shell powder. This is an indication that the composite material has optimum mechanical properties with the addition of 0.9% micro-powder. The increase in the tensile and compressive strength is due to a better interfacial bonding (i.e. two bodies in contact held together by intermolecular forces) which was attributed to the strength of polymer composites. Therefore, the higher values in tensile and compressive strength obtained at 0.9% attributed to the uniform distribution of the periwinkle shell powder into the epoxy resin matrix. Generally, it can be seen from the microstructure that the sample with 0.9% periwinkle shell powder filling gave the best mechanical properties as result of a very good dispersion of the powder fillings. The polymer composite acquired its optimum mechanical strength with the addition of 0.9% periwinkle shell powder. Beyond 0.9%, the composite polymer began to lose its improved mechanical strength. The sharp drop in the mechanical properties as seen in sample with 1% particles fillings may have possibly result from agglomeration due to the presence of excessive periwinkle shell powder in the polymer matrix.

It could be seen from Figure 4.4 that the hardness values of the composite polymer samples increases as the percentage of periwinkle shell powder was increases in the epoxy matrix. The increase in hardness of the polymer composite may be due to an increase in the percentage of the hard elements such as CaO, SiO_2, Fe_2O_3, Al_2O_3, TiO and MgO present in the periwinkle shell powder.

It could be seen from Figure 4.5 that the impact energy (energy absorbed per unit area under the notch) values of the polymer composite samples decreased as the percentage of periwinkle shell

powder in the epoxy matrix. The presence of the hard element and reinforcing with periwinkle shell powder with epoxy play significant role in decreasing the impact strength of the polymer composite.

4.5 ELECTRICAL PROPERTIES

This section introduced results obtained from electrical measurement of pelletized periwinkle shell powder and seven polymer composite samples.

4.5.1 ELECTRICAL PROPERTIES OF PERIWINKLE SHELL POWDER

The real and imaginary parts of the complex permittivity of the pelletized periwinkle shell powder sample are shown in Figure 4.6 and 4.7. The real part of the relative permittivity was observed to be relatively constant from 1 kHz to 50 kHz after which it starts increasing with decrease in frequency. The imaginary part also displayed similar trend. As temperature increases, there occur increases in the real permittivity and decrease in imaginary permittivity. It was also observe that as temperature increases; the acquired negative slope by the imaginary part between frequency of 200 and 900 Hz decrease with increasing temperature.

The behaviour of dielectric properties as a function of frequency in insulating materials (including composites) is governed by dielectric polarization and relaxation effects. The results of dielectric measurements of the pelletized periwinkle shell powder were earlier presented within the frequency range of 200 Hz to 50 kHz. It was observed from Figure 4.6 and 4.7 that at higher frequency (within 1 kHz and 50 kHz), the real and imaginary parts of the relative permittivity were relatively stable. This was identified to be due to interfacial polarization at the electrode-sample interface. This feature was excluded as it is not the characteristics of the sample but a setup measurement error.

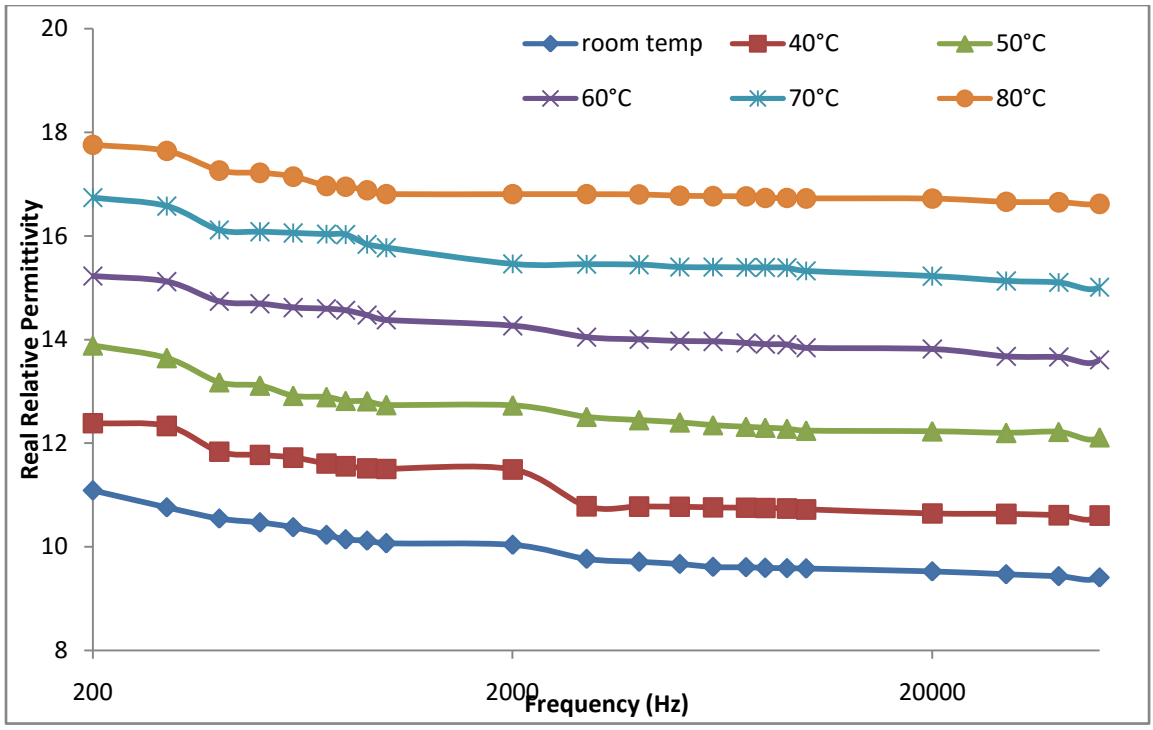


Figure 4.6. Variation of Real part (ε′) of the periwinkle shell powder sample for different temperatures as a function of frequency

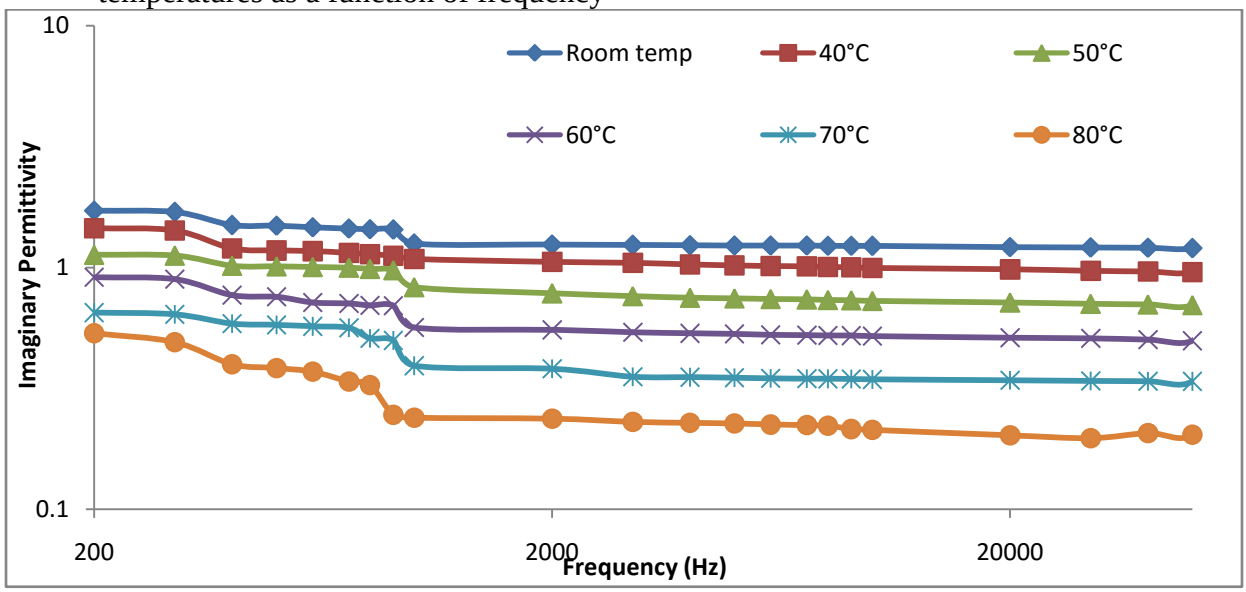


Figure 4.7. Variation of Imaginary part (ε′′) of the periwinkle shell powder sample for different temperatures as a function of frequency

The loss tangent (tan δ) of the periwinkle shell powder sample is shown in Figure 4.8 for frequency range of 200 Hz to 50 kHz. The dielectric response was monitored at different

temperatures from 40 to 80°C. The loss tangent (tan δ) of the periwinkle shell powder sample shows variation in figure 8 as a function of temperatures at room temperatures, 40, 50, 60, 70 and 80°C with frequency range from 200 Hz to 50 kHz. The dielectric loss was observed to have followed a similar pattern as the imaginary part and is relatively constant up to 1 kHz to 50 kHz after which it starts increasing with decrease in frequency. As temperature increases, there occurs decrease in dielectric loss. The log-log plot of electrical conductivity of the sample with frequency in Figure 4.9 revealed that the conductivity was stable up to a certain frequency before it acquired a slope of about 1. The slope was nearly the same at all temperature.The motion of the charged particles in the dielectric material, besides causing conduction current, gives rise to the polarization of the dielectric material.

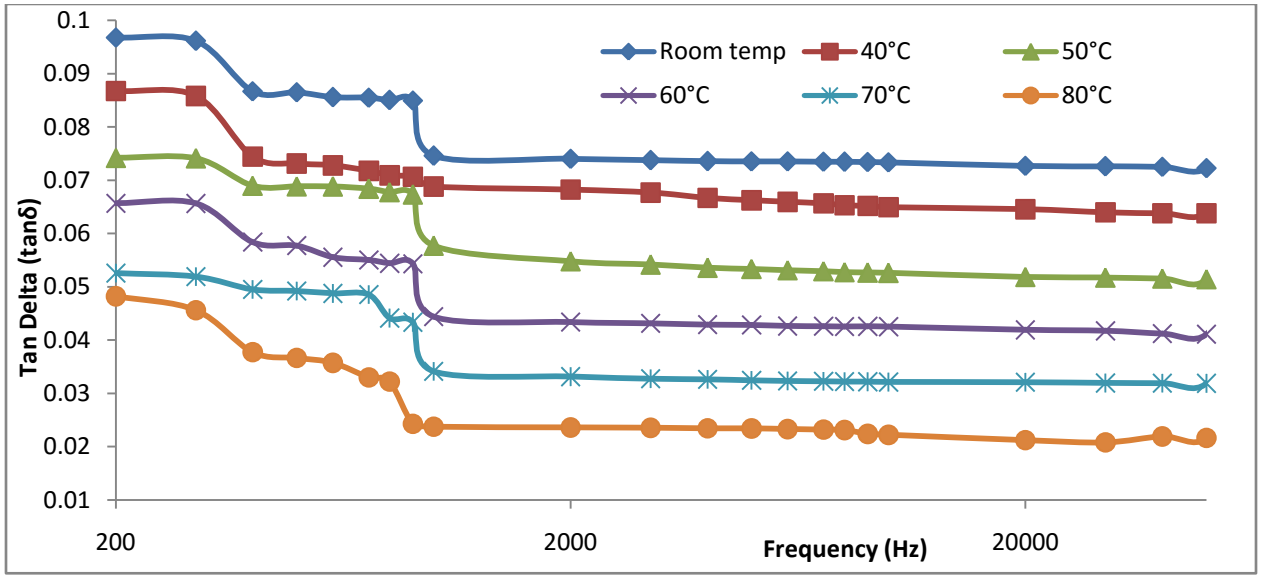


Figure 4.8. Variation of tan δ of the periwinkle shell powder pelletized sample as a function of frequency for different temperatures.

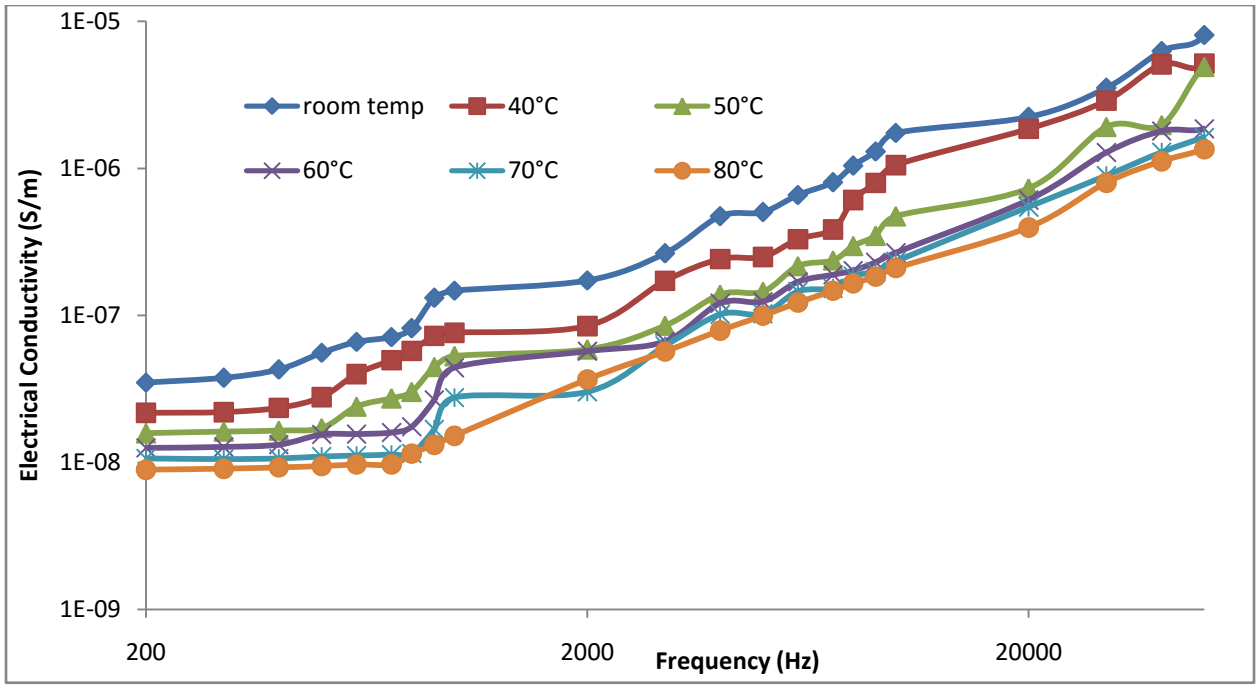


Figure 4.9. Variation of electrical conductivity (σ) of the pelletized periwinkle shell powder sample as a function of frequency for different temperatures

Application of electric field resulted in charge transport and orientation polarization of dipoles in the sample. The electric displacement, *D* that describes the influence of the applied electric field, *E*, on the distribution of charged particle motion and electric dipole reorientation is expressed as

$$D(t) = \varepsilon_0 \varepsilon^* E_0 exp(iwt) \quad (4.1)$$

The decrease in loss tangent with increasing frequency between 200 Hz and 1 kHz is an indication of pure DC conduction. The conductivity beyond 1 kHz is connected with AC conductivity which is a combination of DC conductivity and loss due to polarization. The DC conductivity is likely due to charge transport by electrons `hopping' from donor to donor. It may also be due to negative oxygen ions migrating through the crystal.

When temperature increases, the system entropy increases and that will attempt to randomize the dipoles, thereby counteracting the effect of the applied electric effect. This leads to the reduction in charge transport and polarization and a reduction in the dielectric loss of the sample.

From Figure 4.9, it was observed that as the temperature increases, the electrical conductivity decrease due to the movement of charge carriers in the powder.The constant part which is DC conduction is attributed to charge transport, while the part with a slope is the AC conductivity which is attributed to both charge transport and loss due to polarization processes. The electrical conductivity decreases with an increase in temperature, and the turning point from DC to AC conductivity shifts towards higher frequency as temperature increases. This also showcases the influence of temperature on charge transport and polarization mechanism in the material. Temperature reduced the influence of polarization on the electrical conductivity of the sample thereby extending the frequency range of DC conductivity.

4.5.2 ELECTRICAL PROPERTIES OF POLYMERIC COMPOSITE SAMPLES

The real and imaginary parts of the complex permittivity of the polymer composite samples are shown in Figures 4.10 and 4.11.The dielectric properties of a neat epoxy polymer sample and polymer samples with 0.5, 0.6, 0.7, 0.8, 0.9 and 1% periwinkle shell powder were measured in the ambient temperature variation as indicated. The real part of the relative permittivity of the polymer composite samples was observed to decrease slightly from 200 Hz to 1 kHz, after which it became stable. This constant part is often referred to as the Dielectric constant of the samples. The Dielectric constant of the neat epoxy is 9.502 from Figure 4.10.

Increasing the percentage composition of the powder in the polymer led to an increase in the dielectric constant of the samples. While there is no much significant increase in the value of the dielectric constant of the polymer with powder from 0.5% to 0.8%, 0.9% and 1% periwinkle shell powder shows a more significant increase in dielectric constant value of the polymer. The imaginary part also displayed similar trend as shown in Figure 4.11.

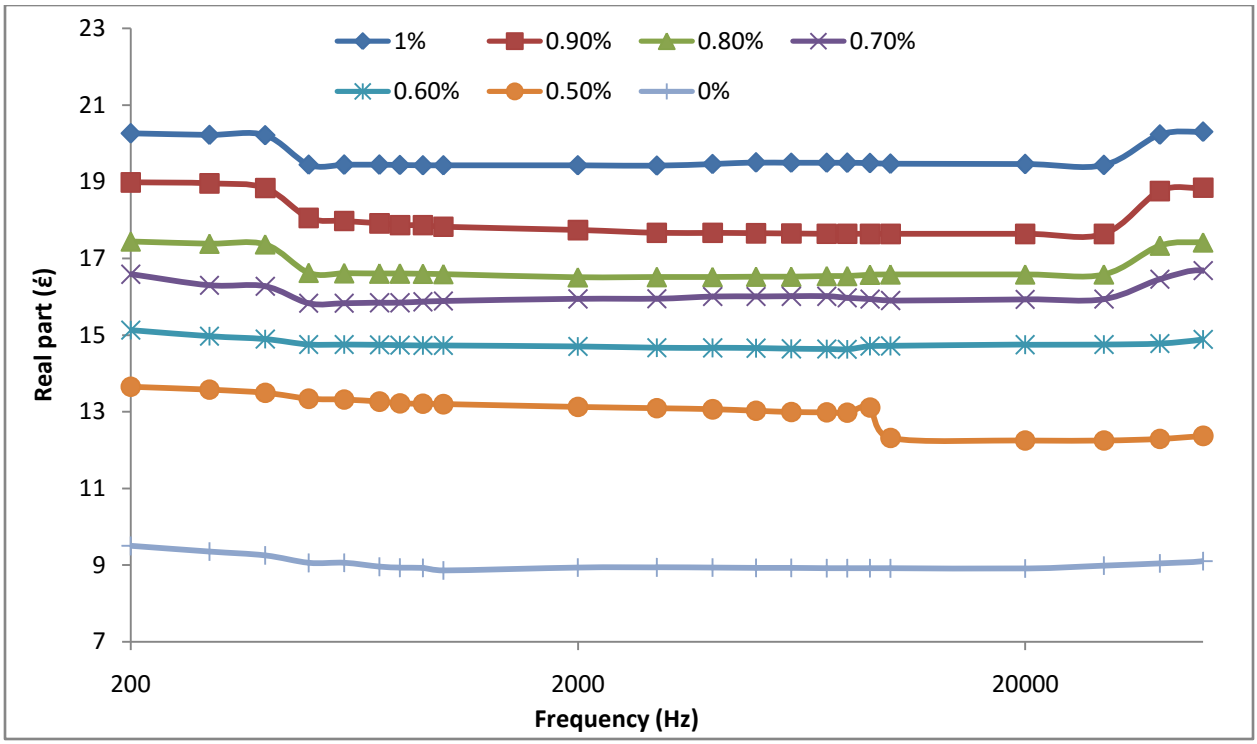


Figure 4.10. Variation of Real permittivity of the polymer microcomposite samples as a function of frequency.

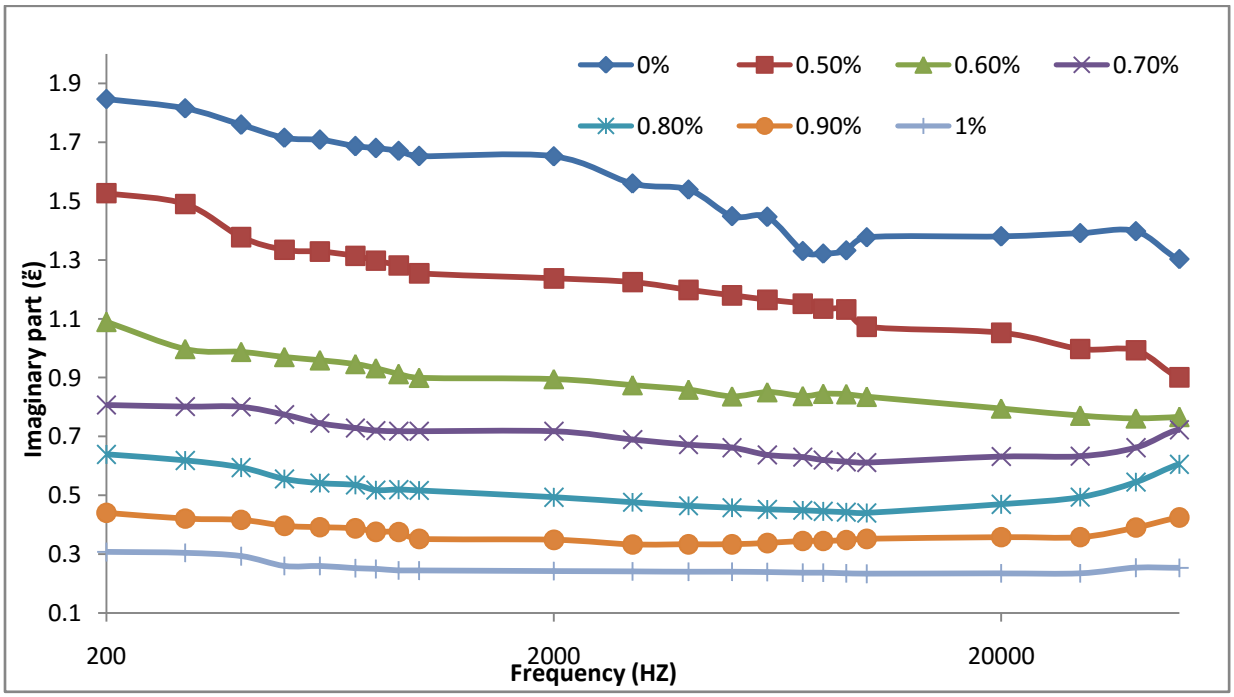


Figure 4.11. Variation of imaginary permittivity of the polymer microcomposite samples as a function of frequency.

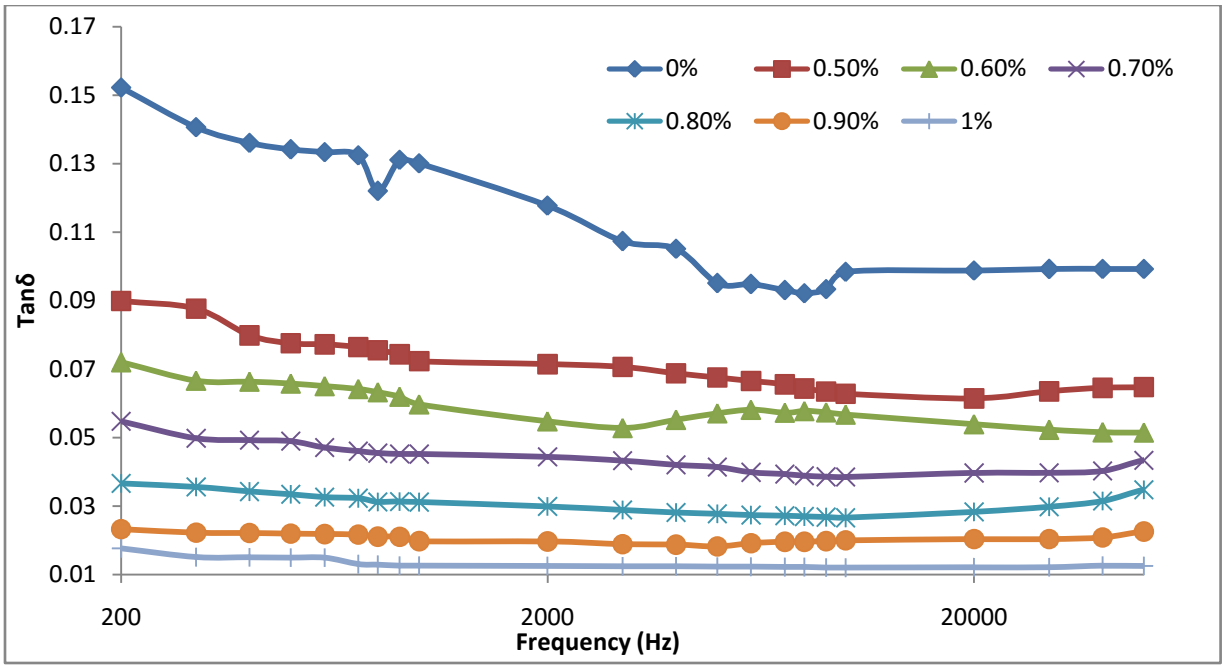


Figure 4.12. Variation of tan δ of the polymer microcomposite samples for different percentages of periwinkle shell powder as a function of frequency.

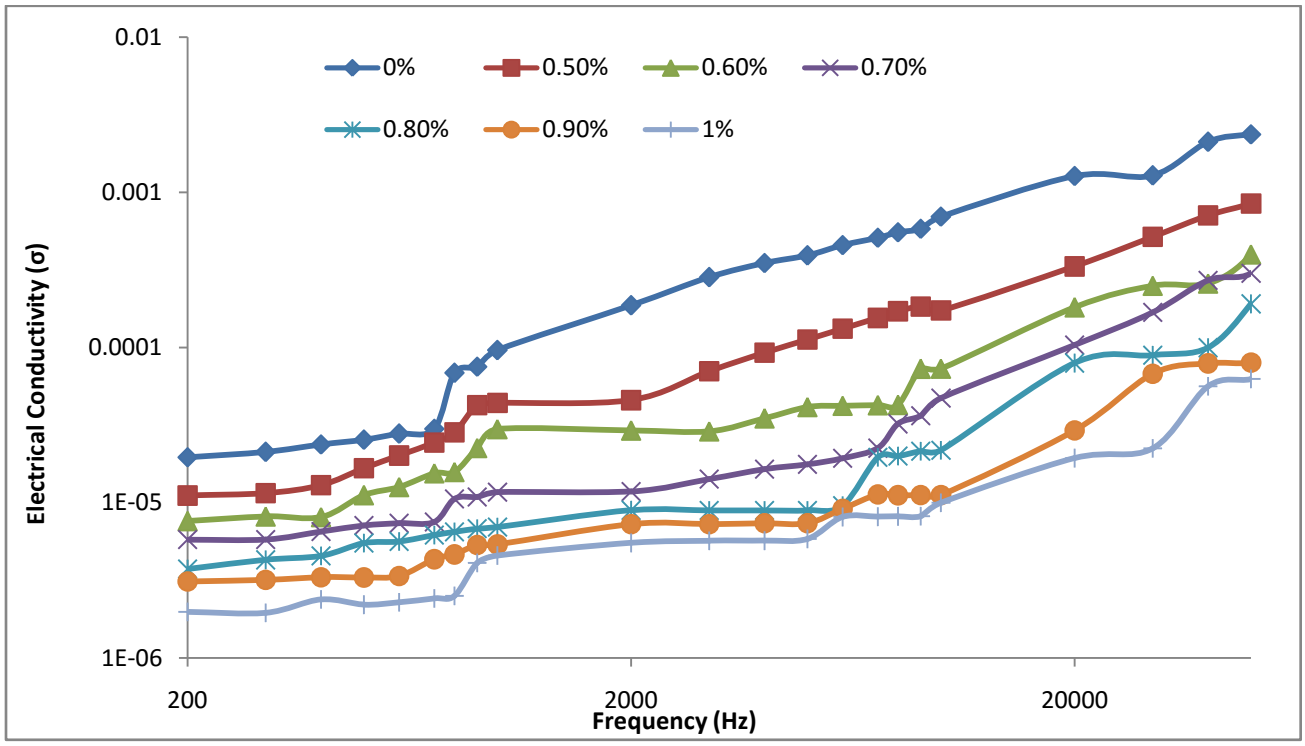


Figure 4.13. Variation of AC electrical conductivity of the polymer microcomposite sample for different percentage of periwinkle shell powders as a function of frequency.

The real and imaginary parts of the complex permittivity of the polymeric composite sample are shown as in Figures 4.10 and 4.11 as a function of frequency range from 200 Hz to 50 kHz at room temperature.

Increasing the percentage composition of the powder in the polymer led to an increase in the dielectric constant of the samples. The addition of 0.5 wt% shell powder resulted in an increase of the dielectric constant to about 5.89. Further increase in the percentage concentration of the powder in the polymer shows a more significant increase in the dielectric constant of the polymer composite. The addition of 0.6 wt.%, 0.7wt.%, 0.8wt.%, 0.9wt.% and 1wt.% periwinkle shell powder produced an epoxy composite with a dielectric constant of 6.65, 7.19, 7.53, 8.01 and 8.83 respectively. A decrease in the imaginary permittivity was observed for all the samples with an increase in frequency from 200 Hz and 50 kHz with slopes higher than that of the dielectric constant. Beyond this frequency, is a steep rise in imaginary permittivity? This is applicable to all the samples.

The occurrence of a (steep) rise in real permittivity and imaginary permittivity at a higher frequency of the dielectric spectra may likely be due to interfacial polarization. Interfacial or space charge polarizations may have occurred due to the accumulation of space charges at the electrode-sample interface. The interfacial phenomenon is an additional polarization mechanism apart from ionic, electronic and dipolar mechanisms in a sample. The shell micro-particles have a large volume fraction of interfaces where interfacial polarization can occur when an electric field of high frequency is applied. Interfacial or space charge polarizations may have also occurred in the samples due to the accumulation of space charges at interface boundaries. The shell microparticles have unmodified surfaces which further enhances the occurrence of interfacial polarization. Meanwhile, interfacial polarization at the electrode-sample interface may have

likely dominated the polarization processes at high frequency, thereby shrouding the effect of polarization due to interface boundaries. The surface treatment of the particles may reduce the interfacial effect.

The tan δ of the polymer composite sample shows in Figure 4.12 as a function of frequency at room temperature. The loss tangent of the epoxy polymer was observed to havedecreased by an order of magnitude with the addition of 1 wt% of periwinkle shellpowder. Reduction in charge transport due to the barrier to the charge transport inpolymers may have resulted in the reduction in loss tangent. This may have beendue to defects, inter-chain charge transport and transport through interfaces. Thepresence of a large number of interfaces in the polymer composite and polymerchain entanglements may have also inhibited the motion of charges in the system,thereby causing the lower loss tangent of the samples studied. The loss tangentspectra picked up a slope at low frequency. This could be attributed to interfacialpolarization. The decrease in the loss tangent due to the addition of the shell powder indicatesa reduction in the dielectric loss of the polymer composite. This is contrary to anearlier reported result where the dispersion of TiO2 microparticles in epoxy led toan increase in dielectric loss. This is an indication that while TiO2 microparticlesact as charge carriers in the polymer matrix, the periwinkle shell powder act as ahindrance to charge carriers transfer. A systematic decrease in tan δ of the polymercomposite was observed with an increase in the percentage composition of theperiwinkle powder.

Figure 4.13 displays the log-log plot of the variation of AC electrical conductivityfor the neat polymer and composite samples at room temperature and within thefrequency range of 200 Hz and 80 kHz. The AC conductivity of all the samples islinearly dependent on the frequency with a slope of 1. The electrical conductivitydecreases with an increase in the percentage composition

of the powder. Theeffective conductivity of the dielectrics is a combination of an AC and DCcomponent of the conductivity.The higher value of the AC conductivity suggests that effective conductivity isdominated by charge transport and dipolar relaxation in the polymer samples andthe effective conductivity decreases with an increase in the percentage compositionof the shell powder. The decrease is due to the scattering of charge carriers in theepoxy, thereby resulting in the reduction of electrical conductivity of the samples.The scattering rate increases with an increase in percentage composition. Theresult is consistent with the decrease in dielectric loss.

CHAPTER FIVE

SUMMARY,CONCLUSIONS AND RECOMMENDATIONS

5.0 SUMMARY

In this research work, assessment of the influence of periwinkle shell powder on some mechanical and dielectric properties of epoxy resin has been studied such as samples preparation, morphology analysis (SEM), elemental composition, characterization of thermal conductivity, mechanical properties (tensile strength, compressive strength, hardness and impact test)and characterization of electrical properties (dielectric constant, electrical conductivity, tan δ, real and imaginary parts of the complex permittivity) of periwinkle shell powder filled epoxy resin are successfully carried out.Microparticle epoxy composite suggested that polymer composite from the waste periwinkle shell is feasible. The waste periwinkle shell can serve as a cheap resource to produce low-cost polymer composite with improved insulation properties for use in high voltage application.

5.1 CONCLUSIONS

Several information are available on the use of periwinkle shell for various applications, but to the best knowledge of the author, no previous work has been reported concerning the possible use of periwinkle shell powder for dielectric application.From the results and discussion the following conclusions can be made:

i. Microparticles powder was produced from periwinkle shell with particle sizes about 4.39 μm to 100 μm size. The elemental analysis of the powder shows that CaO has the highest compositions and constitutes about 81.8% of the total elemental composition.

ii. The thermal conductivity of the Periwinkle shell powder was determined to be17.96 $Wm^{-1}k^{-1}$, a value higher than that of TiO that is often used as filler for polymeric

insulation. It has low loss, low resistivity and a dielectric constant that is comparable to that of CaO.

iii. Polymer composite was successfully prepared from epoxy resin and the periwinkle shell powder with enhanced properties. Microscopic study revealed a uniform distribution of the periwinkle shell powder in the epoxy-based composite.

iv. The mechanical properties of periwinkle shell powder filled epoxy show that, tensile strength of the polymer composites varied from 1.94 MPa to 10. 94 MPa and compressive strength of the polymer composites also varied from 4.31 MPa to 13.73 MPa. The hardness of the polymer composites increased with an increase in the filler content with a maximum hardness of 10.62 and impact strength of the polymer composites decreased with an increase in the filler. This is an indication that the dispersion of periwinkle shell powder has a significant effect on the mechanical strength of the epoxy polymer.

v. The real and imaginary permittivity of the polymer composites at 200 Hz was found to increase and decrease respectively as the powder composition was varied from 0.5wt.% to 1wt.%.

vi. Increasing the percentage composition of the powder in the polymer led to an increase in the dielectric constant of the samples. The decrease in loss tangent and electrical conductivityof the polymer compositeis an indication that the dispersed powder limits the transport of charged particles in the material.

5.2 RECOMMENDATIONS

The following recommendations are offered:

i. Since assessment of the influence of periwinkle shell powder on some mechanical and dielectric properties of epoxy resin has been established, hence the composite has the potential usage in mechanical and dielectric applications.

ii. Since elemental analysis shows that CaO has the highest percentage contained in the periwinkle shell powder, CaO should be usedto ascertain that the dominant metal oxide in the composite powder is responsible for the enhanced mechanical and dielectric properties.

iii. The powder should be processed further to nano-size particles to compare the influence of nanosized periwinkle shell on the polymer matrix with the micro-sized particle used in this work.

iv. The effect of temperature on the epoxy resin/periwinkle shell powder (micropolymeric composite) should be investigated to study the thermally activated processes in the polymer composite.

v. In this research epoxy resin was used as the polymer matrix. Periwinkle shell powder can be used withother polymer typesto prepare compositesand study the impact of the filler on the dielectric properties.

vi. Since the composite materials is intended for high voltage application, high voltage tests such as partial discharge and electrical breakdown study should be performed to evaluate the integrity of the composite materials for high voltage applications.

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APPENDICES

Table A1: Real Permittivity of the Polymer Microcomposite Result

Frequency(Hz)	1%	0.90%	0.80%	0.70%	0.60%	0.50%	0%
200	20.25879	18.98242	17.44233	16.5865	15.13291	13.65471	9.50211
300	20.22293	18.9564	17.38608	16.29817	14.97328	13.57595	9.35443
400	20.21167	18.83615	17.36568	16.27426	14.89803	13.49578	9.255274
500	19.44515	18.05696	16.62518	15.83052	14.75738	13.34107	9.058368
600	19.44163	17.9789	16.61181	15.83122	14.75246	13.31927	9.060478
720	19.44023	17.9135	16.60478	15.84318	14.74473	13.26442	8.959916
800	19.4353	17.8699	16.60408	15.84529	14.73699	13.22011	8.934599
900	19.43108	17.86639	16.59705	15.86779	14.73066	13.20956	8.927567
1000	19.42827	17.82419	16.58861	15.88959	14.72996	13.19761	8.864276
2000	19.42757	17.7384	16.50633	15.94374	14.70534	13.12658	8.938819
3000	19.41983	17.66878	16.51266	15.94796	14.67159	13.09283	8.942335
4000	19.46062	17.66596	16.51547	16.00492	14.66737	13.06399	8.936709
5000	19.49859	17.65612	16.5225	16.00914	14.65823	13.02743	8.93038
6000	19.49648	17.64838	16.52461	16.01125	14.64205	12.99578	8.927567
7200	19.49437	17.64346	16.54079	16.01195	14.63643	12.98594	8.923347
8000	19.49226	17.64065	16.54149	15.97187	14.6294	12.97539	8.921238
9000	19.48383	17.63854	16.57595	15.94023	14.71378	13.11322	8.919831
10000	19.46624	17.63783	16.58017	15.90155	14.718	12.31646	8.918425
20000	19.4571	17.63854	16.58368	15.9339	14.75035	12.25105	8.912799
30000	19.43249	17.63854	16.58017	15.93741	14.75457	12.25246	8.988045
40000	20.22574	18.75668	17.33122	16.45499	14.7827	12.29044	9.04782
50000	20.30169	18.84177	17.41983	16.68143	14.891	12.37131	9.104079
60000	20.36357	19.07736	17.4346	16.2173	15.0654	12.49859	9.25879
72000	20.37201	19.15331	17.47117	16.49015	15.30661	12.68073	9.419128
80000	20.37412	19.3256	18.01547	17.4128	15.50914	12.80661	9.54782
90000	21.15752	19.62096	18.02813	17.77215	15.81786	12.99297	9.720113
100000	21.33544	19.95359	17.95992	18.20113	16.19339	13.27989	10.0007
120000	21.47187	20.24824	18.24684	19.23207	17.18143	14.03938	13.1519
150000	21.99859	21.29184	20.73769	22.05274	19.69339	15.9775	15.02883
180000	21.94937	26.02532	25.64768	27.58368	23.9564	19.87553	18.74895
200000	35.30872	35.45288	35.54008	35.20605	30.53727	25.41842	19.95148

Table A2: Imaginary Permittivity of the Polymer Microcomposite Result

Frequency(Hz)	0%	0.50%	0.60%	0.70%	0.80%	0.90%	1%
200	1.846601	1.527149	1.089418	0.807613	0.639262	0.440962	0.307568
300	1.815607	1.489932	0.99737	0.801812	0.618597	0.421401	0.304759
400	1.759273	1.377638	0.987888	0.801182	0.594775	0.416844	0.293579
500	1.71509	1.334466	0.970741	0.775062	0.556112	0.396711	0.260511
600	1.708124	1.328647	0.959058	0.745492	0.541711	0.3923	0.260264
720	1.686651	1.314065	0.946759	0.728945	0.53567	0.388006	0.253112
800	1.679842	1.297722	0.932557	0.720327	0.518379	0.37634	0.249938
900	1.670583	1.281735	0.912417	0.717859	0.519819	0.375551	0.245415
1000	1.652799	1.254715	0.899526	0.717859	0.516735	0.352206	0.244602
2000	1.652456	1.237501	0.895559	0.717859	0.493704	0.348914	0.243039
3000	1.559781	1.225139	0.874807	0.689909	0.476555	0.33341	0.241583
4000	1.539337	1.19815	0.859199	0.672367	0.464745	0.33371	0.241117
5000	1.44919	1.179872	0.836692	0.662138	0.458334	0.333877	0.240808
6000	1.446244	1.164739	0.851143	0.637728	0.452279	0.338143	0.239612
7200	1.33005	1.151358	0.837935	0.62975	0.449744	0.345283	0.237636
8000	1.322003	1.134577	0.84514	0.620347	0.445959	0.345404	0.237416
9000	1.332399	1.132034	0.843688	0.614496	0.443407	0.348361	0.23517
10000	1.377395	1.073227	0.835099	0.611574	0.440535	0.352404	0.23379
20000	1.38005	1.052582	0.795191	0.632098	0.46965	0.358591	0.235042
30000	1.391524	0.997791	0.771074	0.633193	0.493923	0.358591	0.235522
40000	1.397996	0.993102	0.7619	0.662149	0.545067	0.391077	0.254238
50000	1.303489	0.901413	0.76644	0.722973	0.605688	0.425259	0.253568
60000	1.320046	0.920408	0.777827	0.703669	0.619974	0.435918	0.256377
72000	1.338051	0.955315	0.795331	0.71188	0.62442	0.431907	0.256891
80000	1.3523	0.979174	0.811593	0.796636	0.716655	0.44874	0.265679
90000	1.444815	1.083873	0.862864	0.792283	0.718782	0.496999	0.323075
100000	1.499991	1.225866	1.100503	0.83525	0.760064	0.572069	0.588218
120000	2.223723	1.368138	1.145143	0.911023	0.92402	0.745338	0.777496
150000	2.982772	1.847318	1.672363	1.652853	1.415555	1.552814	1.56036
180000	5.465692	3.508826	4.047434	4.683986	4.109784	6.638277	3.565455
200000	10.96443	9.008036	10.34755	12.03308	11.57079	11.52112	11.56043

Table A3: Tan Delta (Δ) of the Polymer Microcomposite Result

Frequency(Hz)	0%	0.50%	0.60%	0.70%	0.80%	0.90%	1%
200	0.15224	0.08987	0.07199	0.05472	0.03665	0.02323	0.01765
300	0.14064	0.08765	0.06661	0.04981	0.03558	0.02223	0.01507
400	0.13606	0.07985	0.06631	0.04923	0.03425	0.02213	0.01502
500	0.13414	0.07754	0.06578	0.04896	0.03345	0.02197	0.01494
600	0.13334	0.07723	0.06501	0.04709	0.03261	0.02182	0.01493
720	0.13244	0.07645	0.06421	0.04601	0.03226	0.02166	0.01302
800	0.12198	0.07547	0.06328	0.04546	0.03122	0.02106	0.01286
900	0.13112	0.07432	0.06194	0.04524	0.03132	0.02102	0.01263
1000	0.13005	0.07234	0.05971	0.04516	0.03115	0.01976	0.01259
2000	0.11774	0.07142	0.05478	0.04437	0.02991	0.01967	0.01251
3000	0.10733	0.07066	0.05281	0.04326	0.02886	0.01887	0.01244
4000	0.10511	0.06875	0.05517	0.04201	0.02814	0.01872	0.01239
5000	0.09509	0.06754	0.05708	0.04136	0.02774	0.01821	0.01235
6000	0.09479	0.06654	0.05813	0.03983	0.02737	0.01916	0.01229
7200	0.09302	0.06556	0.05725	0.03933	0.02719	0.01957	0.01219
8000	0.09214	0.06432	0.05777	0.03884	0.02696	0.01958	0.01218
9000	0.09332	0.06345	0.05734	0.03855	0.02675	0.01975	0.01207
10000	0.09838	0.06278	0.05674	0.03846	0.02657	0.01998	0.01201
20000	0.09874	0.06143	0.05391	0.03967	0.02832	0.02033	0.01208
30000	0.09919	0.06349	0.05226	0.03973	0.02979	0.02033	0.01212
40000	0.09925	0.06453	0.05154	0.04024	0.03145	0.02085	0.01257
50000	0.09924	0.06478	0.05147	0.04334	0.03477	0.02257	0.01249
60000	0.09937	0.06564	0.05163	0.04339	0.03556	0.02285	0.01259
72000	0.09959	0.06745	0.05196	0.04317	0.03574	0.02255	0.01261
80000	0.09974	0.06865	0.05233	0.04575	0.03978	0.02322	0.01304
90000	0.10749	0.08342	0.05455	0.04458	0.03987	0.02533	0.01527
100000	0.12999	0.09231	0.06796	0.04589	0.04232	0.02867	0.02757
120000	0.16908	0.09745	0.06665	0.04737	0.05064	0.03681	0.03621
150000	0.19847	0.11562	0.08492	0.07495	0.06826	0.07293	0.07093
180000	0.29152	0.17654	0.16895	0.16981	0.16024	0.25507	0.16244
200000	0.39919	0.35439	0.33885	0.34179	0.32557	0.32497	0.32741

Table A4: Electrical Conductivity of the Polymer Microcomposite Result

Frequency (Hz)	0%	0.50%	0.60%	0.70%	0.80%	0.90%	1%
200	1.96E-05	1.11E-05	7.61776E-06	5.79E-06	3.75E-06	3.11E-06	1.99E-06
300	2.12E-05	1.15E-05	8.16809E-06	5.81E-06	4.29E-06	3.19E-06	1.96E-06
400	2.38E-05	1.3E-05	8.09516E-06	6.52E-06	4.56E-06	3.32E-06	2.38E-06
500	2.54E-05	1.67E-05	1.11843E-05	7.15E-06	5.50E-06	3.30E-06	2.20785E-06
600	2.78E-05	2.02E-05	1.26361E-05	7.39E-06	5.63E-06	3.38E-06	2.29E-06
720	3E-05	2.44E-05	1.54878E-05	7.52E-06	6.19256E-06	4.33E-06	2.42E-06
800	6.86E-05	2.84E-05	1.57851E-05	1.06E-05	6.50595E-06	4.65E-06	2.52E-06
900	7.52E-05	4.26E-05	2.2564E-05	1.09E-05	6.80635E-06	5.35E-06	4.10E-06
1000	9.6E-05	4.39E-05	2.98053E-05	1.17E-05	6.97642E-06	5.38836E-06	4.57E-06
2000	0.000187	4.58E-05	2.91716E-05	1.18E-05	8.95208E-06	7.28399E-06	5.52E-06
3000	0.000283	7.05E-05	2.88079E-05	1.42E-05	8.93154E-06	7.29284E-06	5.70E-06
4000	0.00035	9.28E-05	3.49425E-05	1.65E-05	8.93227E-06	7.37999E-06	5.70713E-06
5000	0.000392	0.000113	4.14279E-05	1.77E-05	8.93829E-06	7.39026E-06	5.8522E-06
6000	0.000457	0.000133	4.21579E-05	1.93E-05	9.56052E-06	9.1588E-06	8.10803E-06
7200	0.00051	0.000155	4.24778E-05	2.25E-05	1.96355E-05	1.13085E-05	8.13552E-06
8000	0.000552	0.000171	4.2649E-05	3.22E-05	1.9992E-05	1.1194E-05	8.18274E-06
9000	0.000583	0.000183	7.29148E-05	3.64E-05	2.15193E-05	1.12198E-05	8.20624E-06
10000	0.000697	0.000173	7.31944E-05	4.72E-05	2.1819E-05	1.12294E-05	1.00225E-05
20000	0.001272	0.000333	0.000181578	0.000104	7.94372E-05	2.92536E-05	1.94063E-05
30000	0.001283	0.000517	0.000250072	0.000169	8.91481E-05	6.77593E-05	2.24529E-05
40000	0.00211	0.000711	0.000258612	0.000271	9.97197E-05	7.90867E-05	5.6377E-05
50000	0.002357	0.000845	0.000398562	0.0003	0.000191304	8.01294E-05	6.27545E-05
60000	0.002419	0.001055	0.000961737	0.000539	0.000423564	9.69171E-05	7.5167E-05
72000	0.002511	0.001201	0.001112583	0.00055	0.000456039	9.41038E-05	0.000188085
80000	0.002616	0.001297	0.001167838	0.000686	0.000559814	0.000371099	0.000708737
90000	0.002436	0.001319	0.001206643	0.000858	0.000575719	0.000370439	0.000473758
100000	0.000552	0.001324	0.000519123	0.000869	0.00035811	0.000327903	0.000396565
120000	0.000398	0.001272	0.000330709	0.000391	0.000318013	0.000292264	0.00032782
150000	0.000303	0.000304	0.000302406	0.000314	0.000292966	0.000297874	0.000297114
180000	0.000273	0.000279	0.000261391	0.000268	0.000281223	0.000257215	0.000275395
200000	0.000243	0.000251	0.000249023	0.000255	0.00024117	0.000241927	0.000235836