HYBRID NANOSHELL REINFORCED PLANT FIBER BIOCOMPOSITE.

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KWAZULU-NATAL
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By

Oluwatoyin Joseph Gbadeyan

Student Number: 218088170

September 2020

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Submitted in fulfillment of the academic requirements for the degree of Doctor of Philosophy in Mechanical Engineering. School of Engineering, University of KwaZulu-Natal (Howard College Campus), Durban 4000. South Africa

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Co-supervisor: Prof. Glen Bright

Co-supervisor: Prof. Bruce Sithole

DECLARATION

I declare that the thesis herein submitted to the discipline of Mechanical Engineering, University of KwaZulu-Natal for the award of Doctor of Philosophy in Engineering (Mechanical) is the original work of the candidate and has not been previously submitted for a degree or diploma at any other University or Higher Institution of Education.

--- Date: 28/09/2020______________

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I hereby approve the final submission of the thesis

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PUBLICATIONS

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2. **Gbadeyan O.J,** S. Adali, G. Bright, and B. Sithole, "Physical and Morphological Properties of Snail (*Achatina Fulica*) Shells For Beneficiation Into Biocomposite Materials," Journal of Bio- and Tribo-Corrosion, DOI: 10.1007/s40735-020-0333-6, 2020 (Chapter 3, pages 28-33 in this thesis)

3. **Gbadeyan O.J,** S. Adali, G. Bright, B. Sithole, and S, Onwubu, "Optimization of Milling Procedures for Synthesizing Nano- Caco$_3$ From Achatina Fulica Shell through mechanochemical Techniques", *Journal of Nanomaterials,* vol. 2020, p. 4370172, 2020/07/04, 2020, DOI: 10.1155/2020/4370172. (Chapter 5, pages 42-51 in this thesis)

4. **O. J. Gbadeyan,** S. Adali, G. Bright, B. Sithole, and A. Omojoola, "Studies on the mechanical and absorption properties of *Achatina Fulica* snail and eggshells reinforced composite materials," Composite Structures, p. 112043, 2020/02/05/ 2020. (Chapter 6, pages 52-61 in this thesis)

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ACCEPTED ABSTRACTS FROM THIS STUDY FOR CONFERENCE ORAL PRESENTATION

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DEDICATION

To **God Almighty**

To my late mother, **Comfort Afolabi Gbadeyan**

To My father and mother-in-love, **Rev & Mrs. Ige**

To my loving wife **Omonike** and our precious princesses, **Bethel, Praise and peace**

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ABSTRACT

The production of bio-based composites and nanocomposites, referred to as biocomposites, is vital to mitigate problems caused by the production processes and techniques, limited recyclability, and end-of-life disposal of synthetic fiber-reinforced composites. The sustainable production and use of composites and nanocomposites based on biorefinery concepts are on the topmost agenda of industries seeking green or true biocomposites. Despite considerable advances in the development of biocomposite, large amounts of agricultural wastes are underutilized. How can this waste be beneficiated? In this thesis, a novel hybrid biocomposite material has been developed for utilizing the waste. The development entailed synthesizing a novel nano-calcium carbonate-based material from a snail (*Achatina Fulica)* shell through mechanochemical processes combined with banana fibers and greenpoxy to produce a plant fiber biocomposite. The research work presented in this thesis is, to the best of the author's knowledge, a world-first overall investigation relating to the concept of manufacturing a reinforcing polymer or banana fibers and green epoxy biocomposite reinforced with nano-$CaCO_3$ from *Achatina Fulica* shell. The comprehensive investigation of the hybrid nanoshell and plant fiber biocomposite is done in three phases. In **phase one**, various physical and chemical properties of the *Achatina Fulica* shell were studied. These properties included: microhardness, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX); X-ray diffraction (XRD) spectroscopy; and Thermo-Gravimetric Analysis (TGA). The results showed that the *Achatina Fulica* shell comprises 99.4 % calcium carbonate ($CaCO_3$), exhibits excellent thermal stability with low thermal degradability, high microhardness structure, and high flow strength (tensile) suitable indicators for polymer reinforcement. In **phase two,** the optimization of milling processes for synthesizing calcium carbonate particles from the *Achatina Fulica* shell was studied using mechanochemical ball milling techniques. The milling process was done in two stages: dry-milling followed by wet-milling. Shell particles collected after dry milling were sieved to ≤ 50 μm using a mechanical sieving shaker and then further milled in the presence of different solvents (water, methanol, ethylene glycol, ethanol) to achieve the generation of nano-$CaCO_3$ particles. The characterization of the particles' size and shape by Transmission Electron Microscopy revealed semi-spherical nanoparticles ranging in size from 25.35 nm – 63.68 nm. Chemical characterization showed that solvents used for milling processes have no adverse effect on the chemical properties of the nano-$CaCO_3$ produced. In **phase three**, synthesized $CaCO_3$ particles from snail shells were compared with eggshells at micro and nanoparticle sizes. The particles were doped into polymer composites using conventional resin casting, hand layup, and compression methods to assess the new filler reinforced biocomposite. Separate epoxy composites of snail and eggshell particles with filler content ranging from 5 to 20% by weight, and particle size to ≤ 50 μm, were prepared. The hybrid reinforced snail and eggshell biocomposites exhibited excellent properties in most cases; however, snail shell particle-filled composites exhibited higher mechanical and lower absorption properties than the eggshell particle-filled composite. A study was made on epoxy composites reinforced with nano-$CaCO_3$ particles (1 to 7 wt.% loadings). Test results indicated that loading with snail shell nanoparticles increased neat epoxy tensile strength by 75%, stiffness by over 25%, impact strength by 25%, and hardness by 35%. The improved properties were attributed to homogeneous dispersion and a lower concentration of nano-$CaCO_3$ particles in the composites. Finally, a novel hybrid nanoparticle shell and plant fiber-reinforced biocomposite was developed and investigated. Nano-calcium carbonate ($CaCO_3$) ranging from 1 to 5 wt.% and 20 wt. % banana fiber-filled hybrid biocomposites were prepared using a hand layup process followed by the application of load using a closed mold. The effect of loading 20 wt. % banana fiber of uniform 30mm length on the mechanical, physical, temperature dependant storage modulus, loss modulus, and damping factors of greenpoxy composite were investigated. The loading of banana fiber improved mechanical properties by 40%, negatively affected temperature-dependent properties and water absorptivity. This performance can be attributed to the better load carrying capacity of the fiber and stress distribution within the biocomposites. The hydrophilic nature and poor thermal properties of banana fiber were ascribed to decreased thermal property and higher water absorptivities. Loading of nano-$CaCO_3$ improved most of the banana filled greenpoxy biocomposites, and hybrid composites with 2wt.% nano-$CaCO_3$ exhibited superior properties. Uniform dispersion and excellent matrix/ nano-CaCO3/banana fiber adhesion provided a strong structure that improved mechanical, thermal, and physical properties.

In conclusion, work in this thesis has demonstrated that waste snail shells can be beneficiated via the production of hybrid biocomposite materials incorporated with nanoparticles generated from the shells. This study is novel work that has not been previously reported in the literature and has generated 6 publications in high-impact journals.

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CHAPTER ONE: INTRODUCTION

1.1 BACKGROUND

The application of polymer-matrix reinforcement, such as fillers for plastics or non-woven materials usage, has increased in the automotive industry over the decades. In this material system, fibers are constituents that fulfill the structural function in nature. Synthetic fibers such as glass, aramid, carbon, and graphite are commonly used as reinforcement in the selected polymer matrix [1]. These fibers' tremendous strength and stiffness make them one of the most suitable reinforcements to improve strength. Most engineering industries adopt the material produced from the combination of the constituents mentioned above called "composite."

Consequently, synthetic reinforced composite materials became an ideal replacement for traditional engineering materials such as metals, metal alloys, and ceramics [2]. The composite materials' unique properties made them suitable for applications in various structures and eventually increased their users globally. According to Shah et al. [3], fiber-reinforced plastics (FRPs) ' total global production was over 5.9 million tonnes in 1999 and increased in 2011 to 8.7 million.

The increase in consumption of FRPs raised concern towards environmental and sustainable issues, which related but not limited to the energy-intensive and unsustainable production processes of the reinforcing synthetic fibers and plastics. Limited recyclability and end-of-life disposal options of FRPs were also identified [4, 5]. These issues led to stringent government legislation in the EU, which became barriers to developing or even continued use of FRPs in some global markets.

To alleviate the aforementioned challenges, materials from renewable resources are being developed to replace the reinforcing fibers and the polymer matrix for composites development. These materials produced a beneficial environmental composite with various cellulose fibers known as natural fiber-reinforced composite [6-12]. According to Joshi et al. and chin [13, 14], natural fiber composites are most likely to be environmentally superior to glass fiber composites in most cases for the following reasons: (1) natural fiber production has lower environmental impacts compared to glass fiber production; (2) natural fiber composites have higher fiber content for equivalent performance, reducing more polluting base polymer content; (3) the lightweight natural fiber composites improve fuel efficiency and reduce emissions in the use phase of the component, especially in auto applications [15]; and (4) end of life incineration of natural fibers results in recovered energy and carbon credits [5, 14, 16].

As mentioned earlier, these reasons made natural-fiber-reinforced composites one of the most promising sectors for part development in automotive, both for applications and tonnage, most especially structural automotive parts or engineered parts. This sector has undoubtedly been the most technically advanced one and a source of many uses for non-woven products and compounds, including parcel shelves, boot trim panels, under-the-hood parts, structural parts, Class A parts, and dashboards. However, the principal challenge includes but is not limited to information about these materials, their properties, their current and potential applications, and their processing requirements. This research focuses on the area mentioned above to investigate hybrid nano-shell and banana fiber-filled composite properties, analyze research data, and recommend their applications.

It is well known that there are several natural fibers. Therefore, natural fiber was classified into a sub-group to understand their nature, origin, and sub-group of the fiber. Natural fiber has been classified into three major groups according to origin. For example, animal fibers come from animal hair; for example, wool fibers; are produced by silkworms or extracted from bird feathers. Plant fibers can be divided into sub-classes: 1) wood fibers and 2) crop fibers, which consist of seed fibers such as cotton or kapok; bast fibers such as banana, flax, hemp, jute, and ramie; leaf fibers such as sisal; stalk fibers such as bamboo and alpaca; or fruit fibers such as coir [17]. While animal fibers consist of proteins, plant fibers are made up of cellulose fibrils (very high tensile strength) embedded in a hemicellulose and lignin matrix.

Natural fibers/fillers possess numerous advantages, including high biodegradability, low CO2 emissions, high thermal and sound insulation properties, and outstanding specific modulus. On average, natural fibers are less expensive than synthetic fibers, although natural fibers vary widely as a function of type [18]. Meyers et al. [19] established that most natural (or biological) materials are complex composites whose mechanical properties are often outstanding, considering the weak constituents they are assembled. Furthermore, natural fibers possess high specific modulus, low cost, lightweight, biodegradability, lower energy requirements-less wear and wide availability, resistance to deforestation along with other usual advantages [20]. Additionally, the easy recycling or disposal of this biodegradable material at the end of its life without negatively harming the environment makes it more preferable to synthetic fiber. These complex structures, which have risen from hundreds of million years of evolution, are the main inspiration for developing these present novel materials.

As suggested by the present study, the combination of natural source fiber for hybrid composite will produce cheaper material and provide biodegradable and green material. Moreover, research clearly shown that many natural fibers are yet to be sourced because there is limited information about them. For example, despite rigorous research on natural fiber, animal shells such as snail shells have not been explored adequately. Numerous research work has been done on the shell, most notably on eggshell [21-23]. Onwubu et al. [23]. reported the physicochemical characteristics of an eggshell-based dental abrasive material, and the result showed that eggshell offered required properties that made it suitable for dental abrasive material. This research was, however, limited to the abrasiveness aspect of eggshells.

Mohan and Kanny [21] took it further by using eggshells as a nano-filled and investigate the thermal, mechanical, and physical properties of nano-eggshell particle-filled epoxy nanocomposites. The research output shows that composite has an optimum mechanical property at 2 wt.% nano-egg shell filler concentration. This yield depicted the efficiency of nano-eggshell in enhancing the mechanical properties of composite material. However, more research work needed to be done in thermal properties, hybrid composite with fiber. Furthermore, most of the research on other shells is limited to shell chemical composition, development, and mechanisms [19]. Also, numerous snail species have tougher and stronger shells, which reinforcement properties are not exploited fully. The snail species such as *Achatina Fulica* (Giant Africa land snail), *Achatina Achatina*, and *Achatina Marginata* with tougher shells have not been exploited at nanoparticles. [24, 25].

The present work investigates individual constituent properties of *Achatina Fulica* (Giant Africa land snail) and banana fiber, studies their synergistic properties of the hybrid composite constituting natural fibers/filler and provides recommendations for where the material is applicable.

1.2 PROBLEM STATEMENT

Factors such as cost, limited recyclability, and end-of-life disposal issues of synthetic fiber-reinforced composite have raised concerns. These factors harm both the ecosystem and human well-being. Deteriorated particles from synthetic fiber-based composite washed to streams or rivers or exposed to the atmosphere often harm human health and kill aquatic animals [26, 27]. This discovery led to a massive reduction in the development and continuous usage of this material in the United Kingdom and the United States. To alleviate this problem, biobased and environmentally friendly materials were sourced. Among the materials sourced, natural fibers are the most suitable; however, the natural materials readily available are underutilized.

Additionally, limited information is available on those that are readily sourced. Numerous natural materials have been investigated and confirmed fit for composite reinforcement application. However, most of these fibers are underutilized. Underutilization of agricultural waste with potential reinforcement properties for natural fiber composite development motivates this study.

1.3 AIMS

This study aims to investigate properties of *Achatina Fulica* shell, synthesized micro, and nanoparticle from *Achatina Fulica* shell, develop and investigate the properties of shell particles filled composite, biocomposite and banana fiber, and nano-shell filled hybrid biocomposite

1.4 OBJECTIVES

Research Objectives: The objectives of this study are:

To determine the physical, thermal, and chemical properties of the *Achatina Fulica* shell.

To optimize milling procedures for synthesizing calcium carbonate particles from the *Achatina Fulica* shell using mechanochemical ball milling techniques.

To fabricate and investigate the properties of composite filled with $CaCO_3$ microparticles synthesized from *Achatina Fulica* shell and evaluate with properties of composite reinforced with eggshell microparticle.

To develop and investigate properties of nanocomposite filled with different loading nano-$CaCO_3$ synthesized from *Achatina Fulica* shell.

To fabricate and investigate properties of hybrid nano-shell reinforced plant fiber biocomposite.

1.5 SCOPE OF THE WORK

This research is based on experimental work. The suitability of hybrid nano-shell reinforced plant fiber biocomposite as a potential filler, its composite structural formation, toughening mechanism, and failure mechanism associated with this research evaluation are focused on the following areas:

(a) Characterization of snail shell powder at different particle sizes
(b) Evaluation of the snail-shell particle reinforcement effectiveness on the improvement of composite properties.
(c) Characterization of hybrid nano-shell reinforced plant fiber biocomposite laminate.
(d) Evaluation of the damage behavior of hybrid nano-shell reinforced plant fiber biocomposite laminate subjected to quasi-static loading.
(e) Shell particle in matrix distribution evaluation using a scanning electron microscope (SEM), transmission electron microscope (TEM), and thermo-gravimetric analysis equipment (TGA/DSC) was used to determine material thermal stability and degradation.

(f) Detailed microscopic analysis of the polymer nanocomposite and fracture of hybrid nano-shell reinforced plant fiber biocomposite analyzed under scanning electron microscopy (SEM)

1.6 STRUCTURE OF THE THESIS

The thesis is separated into ten chapters. Chapter 1 introduces the concerns rising from adverse effects of energy-intensive and unsustainable production processes of the reinforcing synthetic fiber on environmental sustainability and ecosystem. It shows the importance of the problems and the significance of the solutions. In this regard, Chapter 2 provides an overview of the solution contributed by other research to solving these concerns. Subsequently, the introduction and review of several combinations of biobased polymetric polymer, suitable filler, and fiber, synthesized with advanced methods and techniques to develop biocomposite, follows. Then, Chapter 3 presents the microhardness, and flow strength (tensile) of a shell of an African Giant snail (*Achatina Fulica*) measured as a function of indentation load. The influence of loading direction on the hardness of the shell material's nacreous and prismatic structure was analyzed through a microstructural study.

Furthermore, Chapter 4 presents the functional group, elemental composition, carbonate ion, and mineral deposits in the shell used for this study. It also gives the shell's thermal stability and material degradation to complement the physical and microstructure study reported in Chapter 3. Subsequently, Chapter 5 presents synthesizing calcium carbonate nanoparticles from the *Achatina Fulica* shell through mechanochemical techniques. It also presents the milling processes adopted for milling shells into micro and nanoparticles used as a modifying filler in this study, after milling the *Achatina Fulica* shell into a particle size $\leq 50\mu m$. Chapter 6 focuses on the mechanical and absorption properties of composites reinforced by *Achatina Fulica snail* (S-shell) and eggshell (E-shell) microparticles (50µm). Chapter 7 provides information on investigating the reinforcement properties of nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell through mechanochemical methods on epoxy nanocomposite. And chapter 8 presents the "Mechanical, Microstructure, and dynamic mechanical properties of hybrid nano-shell plant fiber biocomposite. Chapters 5, 6, 7, and 8 provide information on how bionanocomposite and hybrid with different combinations of biobased polymer, micro/nano-$CaCO_3$, and banana fibers were developed and investigated. The properties of bionanocomposite and hybrid, such as mechanical, chemical, and thermal properties, were investigated, reported, and compared with the available literature in the same research area. Chapter 9 presents conclusions drawn from the study. It also identifies limitations and considers future directions for this research, and Chapter 10 gives references used for this study

CHAPTER 2- NANOFILLER/NATURAL FIBER FILLED POLYMER HYBRID COMPOSITE: A REVIEW

The chapter represents the actual paper submitted to the International Journal of Engineering science and Technology Review.

Author contribution:

Gbadeyan O.J *conducted a comprehensive review and gathered information on composite material development, challenges, and the effort invested in solving these challenges, biocomposite development, and applications. He developed this manuscript based on sourced information.*

Professor S. Adali, Professor G. Bright, and Professor B. Sithole *contribute to this manuscript by providing information on the searching website, proofreading the manuscript, and suggesting journals where the manuscript was submitted.*

2.1 OVERVIEW

In this chapter, the literature on both composite and bio-composite is reviewed. It is structured into four main sections: fillers (animal shells), reinforcement (natural fibers), biobased polymer, and biocomposite. The first section describes numerous sources, uses, and characteristics of shells. In the second section, different natural fibers, their structures, and their properties are given. Section three describes the applications, synthesis, and characterization of a biobased polymer. Finally, a depiction of hybrid biocomposite is specified.

2.2 INTRODUCTION

The development of new materials with new required properties for a specific application by combining different materials known as composite is becoming more attractive. This attractiveness is because composite is not found directly but formed through engineering [28-30]. The final product developed from combining two or more material constituents with different properties often results in a lightweight structure having superior stiffness and tailored properties for a specific application, where saving weight, better strength, and reduced energy are required [31]. It is well known that the two main components of composite are matrix, and fiber serves as a reinforcement, and the matrix serves as a binder that bonds fibers together to form a composite. Matrix imparts rigidity to composite, which aids reinforcement strength for supporting high tensile loads [20, 32].

In the composite system, fiber often serves as load-carrying mechanisms that apply stress on composite most times, resulting in transferring loads from one fiber to another, glued together in a matrix. Matrix stiffness commonly accompanies brittleness; however, the combination of matrix and fiber produces a final composite with superior properties for specific applications. This composite may fail through different mechanisms, including but not limited to brittle cracking, extensive loading of fiber-matrix [33]. The limited amount of matrix at the fiber interface and fiber orientations may also be related to composite failure

The introduction of organic or inorganic fillers to composite has been proved to provide solutions to the above-mentioned composite failure challenges and be an effective way to improve the mechanical strength and stiffness of materials [31, 33, 34]. However, the effectiveness of filler loading on composite properties development often depends on the volume or percentage adopted [33]. Based on tremendous existing knowledge and experience derived from synthetic fiber composite characterization, the mechanical behavior of bio-composite has been studied. Naturally sourced fibers from plant and animal fiber composites have been widely investigated. Several research studies have provided information on mechanical properties such as impact, flexural, and tensile properties of plant fibers composite [14, 20, 29-31]. These plant fibers studied include but are not limited to sisal, hemp, jute, pineapple, and coir.

According to Brouwer [35], composite has been used far back in the ancient days. Beginning about 3000 years ago, Egyptians combined straw and clay in composite systems to build walls. In this case, straw was used as reinforcement, while clay serves as both filler and matrix when water is introduced. The strength and stiffness offered by the final material result in fast development and composite usage, which led to an increase in synthetic composites' production in 1940 [36], and still on to date. However, growing in the realization of the interconnectivity of global factors show a gap for producing a sustainable and environmentally friendly composite. These factors include but are not limited to eco-efficiency, the principle of sustainability, green chemistry, industrial ecology, and engineering are being incorporated into the development of new materials, processes, and products for immediate and next generations [32, 36, 37].

2.3 BIOCOMPOSITES

The stimulated awareness relating to the energy-intensive and unsustainable production processes of the reinforcing synthetic fibers and plastics triggered stringent policies to end the continued usage of fiber reinforcement polymer (FRPs) in the EU [13, 15]. Furthermore, limited recyclability and end-of-life disposal options of FRPs raised several concerns. These concerns become barriers to synthetic fiber-filled composite development because of the catastrophic destruction they have on the ecosystem [32, 38]. The integrated manufacturing composite policies provided composite science and genetic engineering processes with safe strategies to protect our environment. These policies offer significant opportunities for developing materials from biobased resources that support global sustainability [30, 31].

Composite materials, especially biocomposites from bio-fibers, bio-fillers, and bio-polymers, are considered one of the most suitable global sustainability shifts. These bio-materials are extracted from renewable agricultural and forestry feedstocks, including wood, agricultural waste, grasses, and natural plant fibers. The final biocomposite produced from combining these fibers/fillers have been used for industrial products for durable goods applications. Biocomposite can be used alone or combine with other materials as a compliment. The exciting aspect of composite materials is that they can be tailored, modified, and designed to meet several application requirements.

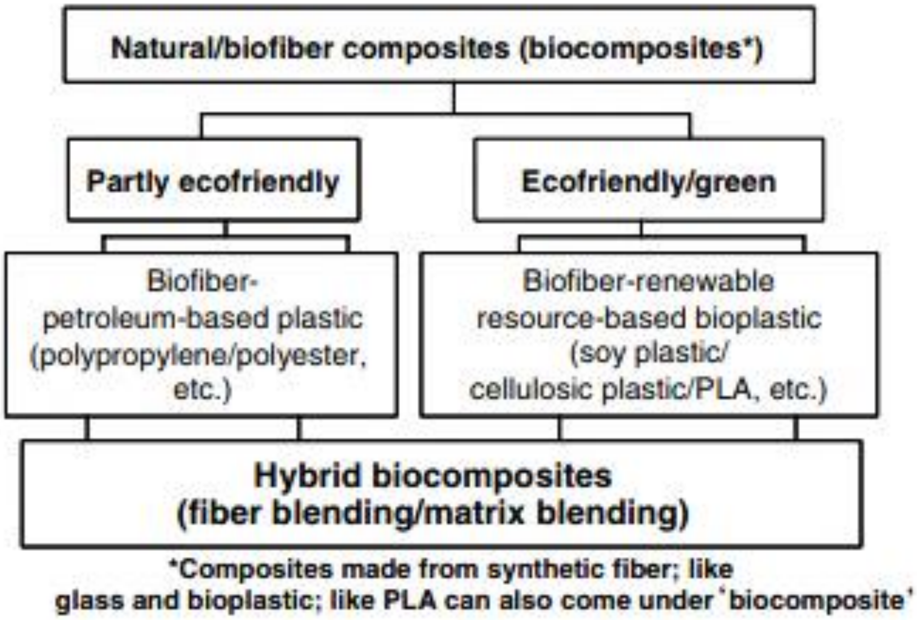

Figure 2.1: Classification of bio-composite [37, 39]

Additionally, since natural fibers are recyclable, biodegradable, and cheap, biocomposite can be manufactured from a renewable source, making it possible to develop non-toxic and environmentally friendly materials. This motivation surely helps in reducing environmental problems. The development of biocomposite has increased the high-tech revolution in recent decades, also served as a response to an increase in the quest for the development of recyclable, sustainable, and biobased materials. Combining bio-based matrix and natural plant fibers have been proved to produce a low-cost composite with the constituents' genetic properties.

Material composed of natural/bio-filter or fibers and bio-based resin is a viable alternative to fiberglass composite, predominantly in building, packaging, and automotive application. Likewise, food product industries draw more interest in using biobased material because polythene contains toxic elements linked to cancer [40]. It has also become one of the fastest-growing additives for thermoplastic and thermosetting polymers [37, 41, 42]. Recent enhancements in bio-composite development have offered researchers opportunities to developed several biobased composites [14, 43-46]. The stiffness and strength of reinforced fibers and matrices suitable for bio-composite development have been studied extensively [43, 45, 47-53]. However, the incompatible nature of fibers hydrophilic and hydrophobic matrix combined harm fiber-matrix adhesion, resulting in poor mechanical properties. Several investigations have been conducted to solve compatibility, wetting this fiber by matrix, loading optimization, and critical length of the filler/fiber, which eventually affect the final composite material's strength and stiffness [54-56].

Andersons et al.[57] investigated flax and thermoplastic matrix composites for determining the strength and stiffness of composite material under uniaxial tension. This study affirmed that relative fiber length determines the strength model's sensitivity to the matrix and adhesion properties. This discovery suggested that a more sophisticated strength model such as critical fiber length and loading optimization should be considered in this case. With this understanding, Awal et al. [58] developed biocomposite fiber from the combination of wood pulp and polypropylene (PP) using the extraction process.

The generated fiber was investigated to understand the nature of wood pulp reinforcement relations with a polypropylene matrix. The results show that fiber length lies between 0.2-1.0 mm, classified as critical length for the study. A favorable fiber-matrix adhesion and chemical linkage for improved strength were observed. This outcome shows that compatibility, critical length of the fiber, and fiber-matrix adhesion play a significant role in improving mechanical strength and stiffness of biocomposite.

2.4 APPLICATIONS OF BIOCOMPOSITES

Environmental sustainability, eco-friendly, green chemistry, and industrial ecology offered by natural composites, known as biocomposite, are controlling the manufacturing of next-generation materials, processes, and products [59]. The increase in global environmental, high percentage collapse of petroleum resources, and social concern brought biocomposite to the limelight. Similarly, innovative eco-friendly regulations have pushed for the search for new composites compatible with the environment. In searching for suitable material, biocomposite was found to be one of the most suitable. This discovery has drastically increased the use of biocomposite materials in different sectors over the past decades. These sectors include but are not limited to the domestic sector, aerospace industries, circuit boards, mass transit, and automobile interior applications [60]. However, biocomposite products are limited in some other sectors due to low mechanical strength [59]. This challenge consequently generated several kinds of research on improving the mechanical strength of biocomposite [61-67].

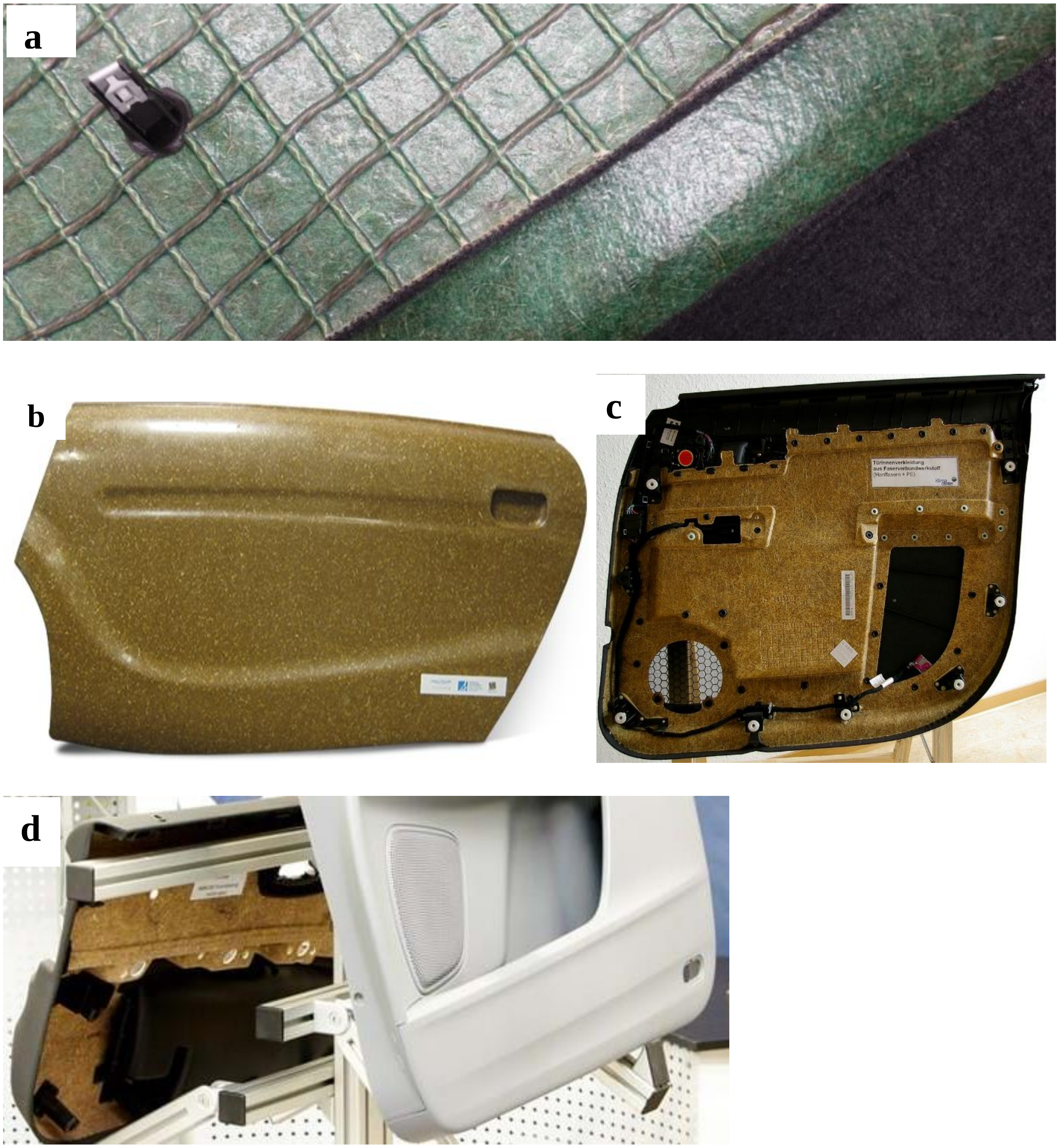

Figure 2.2: Biocomposite made for automobile interior part: (A) powerRibs reinforcing automotive interior parts in Volvo Cars [64] (B) Window panel [65] (C) Interior carpeting [66] and (C) Door [67]

In this regard, several types of natural fibers from different sources have been investigated. These fibers are incorporated into polymer matrices to fabricate composite materials that exhibit strength and stiffness that can contend with synthetic fiber-based composites' mechanical properties. The result of rigorous research for inexpensive and alternative fiber led to discovering agricultural waste such as plant leaf, bark, and fiber composites. Bharath et al.[60] confirmed that fiber extracted from agricultural wastes could be used to develop fiber-reinforced polymer composites for commercial use and have considerable market demand. The materials produced from the aforementioned natural-fiber-reinforced composites are among the most promising sectors for part development in automotive, both for applications and tonnage, especially structural automotive parts or engineered parts. This area is where many applications for non-woven products and compounds are utilized and most technically advanced. Products engineered from these materials include package shelves, Class A parts, boot trim panels, window panels, as shown in Figure 2.2, under-the-hood parts, structural parts, and dashboards. The major challenge is to provide more information about these materials, their properties, their processing requirements, and potential applications.

Moreover, these biocomposite materials are only affordable but also reduce automobile net weight. Volvo car affirmed that usage of power-rids reinforced biocomposite shown in Figure A could not only used in a wide range of semi-structural interior parts but instantaneously reduce up to 50% weight when related to current standard engineering plastics [68].

Michael Carus, Managing Director of the Nova-Institute from Hürth, Germany, one of the notable exhibitors specializing in biocomposites, acknowledged the optimistic projection at which this composite is developed and used for various manufacturing applications. In 2012, 350,000 tonnes of wood and natural fibers reinforced biocomposite products were produced by more than 100 companies in Europe. The majority of these products were manufactured from wood flour and wood fibers (wood-plastic composite) using extrusion techniques. European automobile manufacturers used over 90,000 tonnes of these natural fiber composite. As of 2014, both wood-plastic (WPC) and natural fibers biocomposites (NFC) shares stretch to above 15 % of the total composites market [69].

A review conducted by Amar et al. [37] confirmed that the production of materials and chemicals from biobased feedstock is estimated to rise from 15% ~18% in 2020 and ~25% in 2030. Anticipations are that renewable resources could be the base materials for two-thirds of the $1.5 trillion global chemical industry production. Due to this, the United States forestry, agricultural, chemical communities, and life sciences established tactical visions for using plants and agricultural remains to produce industrial products and identified the main barriers encountered during implementation. Technology measures such as Road Map for Plant/Crop-based Renewable Resources 2020, established by the U.S. Department of Agriculture (USDA), as well as the U.S. Department of Energy (DOE), was put in place to target 10% of basic chemical building blocks ascending from plant-derived renewables by 2020. They plan to achieve more growth through these ideas, targeting 50% by 2050 [37]. This idea provides more information about how the natural fiber market is growing. It is also evident that the development of natural fibers reinforced biocomposite products is becoming an effective way to improve the economy. These facts are eventually the drive and motivation behind the development of hybrid nano-shell biocomposite.

It is well known that biocomposite is the combination of matrix and natural fiber. Hence, the following section discussed natural fiber.

2.5 NATURAL FIBERS

Natural plant fibers are made up of lignin and cellulose, protein, vegetable oil, and carbohydrates such as sugars and starch. These constituents are often used for producing new materials and chemical products [38]. Furthermore, these green materials possess environmental benefits with various cellulose and fibers suitable for fabricating filler /fiber-reinforced composite [6-12].

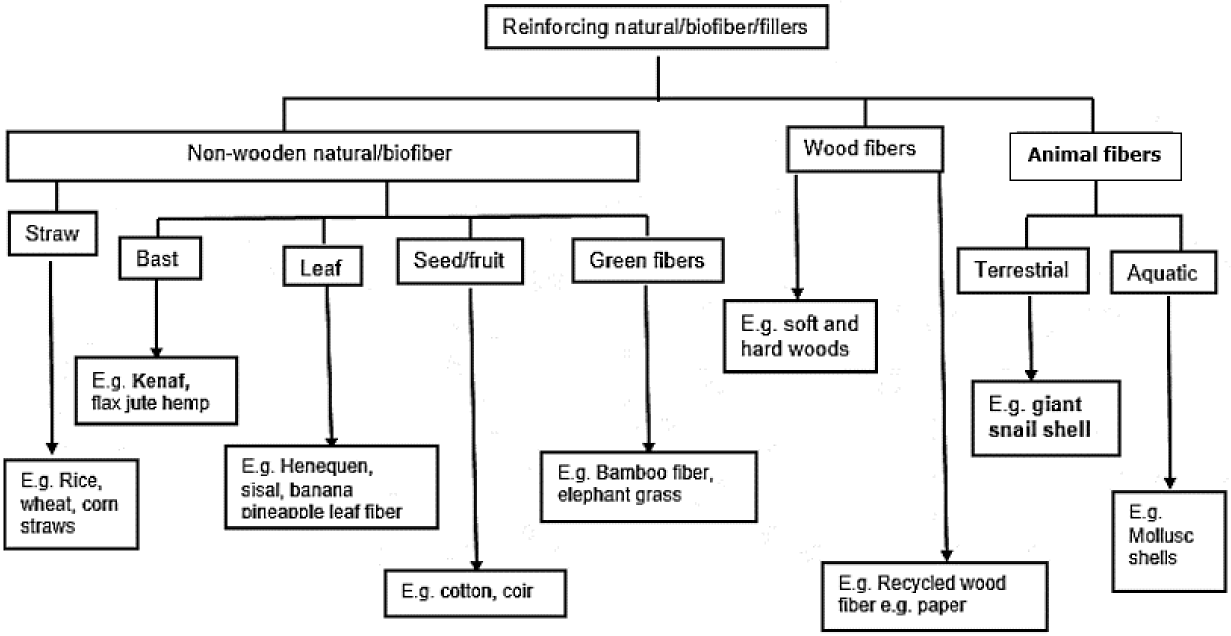

Figure 2.3: Modified schematic classification of natural fibers and fillers [37]

According to Joshi et al. [13], natural fiber-based composites are mostly expected to be environmentally friendly than synthetic fiber-based composites in most cases due to the following reasons:

(i) Manufacturing of natural fiber often has lower environmental impacts than glass fiber production;
(ii) Higher fiber loading of natural fiber, which equivalent to performance, reduces the amount of more polluting base polymer composite;
(iii) The usage of lightweight natural fiber composites, particularly in automobile industries, helps in fuel efficiency and reduces emissions in the use phase of the component, [15]; and
(iv) (iv) Consequently, end-of-life disposal of natural fibers results in improved energy and carbon acknowledgments [5, 16].

Natural fibers' main advantages include but are not limited to excellent acoustic insulation characteristics, high biodegradability, low CO2 emissions, and exceptional specific modulus. On average, natural fibers are cheaper compared to synthetic fibers. The price of natural fibers depends on the functionality of the fiber type [18]. Meyers et al. [19] established that natural (or biological) materials are complex composites having outstanding mechanical properties when considering the weaker components from which they are assembled.

The complex structure formation of natural fiber becomes an inspiring material component for Researchers in designing novel materials. However, natural fiber has drawbacks, including high moisture, low modulus, disintegration in a biological attack, alkaline absorption, and inconsistent physical and mechanical properties. One of the identified solutions to all these difficulties is the fiber's chemical treatment [70, 71]. The chemical treatment is deliberated in the subsequent section.

2.5.1 Classification and Structure of natural fibers

It is well known that there are several kinds of natural fibers. In this regard, natural fiber is classified into sub-groups better to understand their nature, origin, and sub-group. Naturally sourced fibers are categorized into two main groups in harmony with their background: plant and animal fibers. For example, animal fibers come from animal hair, wool fibers; they are produced by silkworms or extracted from bird feathers. Furthermore, nanofiller of a different particle could be produced from mollusk and terrestrial snail shells, bones, and horns. Plant fibers can be divided into sub-groups: 1) wood fibers and 2) crop fibers made of seed fibers such as cotton or kapok. Bast fibers such as hemp, flax, hemp, ramie, and jute; leaf fibers such as sisal and pineapple; stalk fibers such as bamboo, banana, and alpaca; or fruit fibers coir are primarily used [17]. Although animal fibers consist of proteins, plant fibers are comprised of cellulose fibrils exhibiting a very high tensile strength embedded in hemicellulose and lignin matrix.

Moreover, studies have shown that natural fibers, both animal and plant fibers, are composed of parts that may reinforce composite material [72-74]. However, a plant fiber with cellulose is stiffer and tougher than animal fiber. Therefore, plant fiber or both, where animal fiber serves as filler, may have a strong structure suitable for biocomposite development. Given this, this study focuses on the combination of both fibers. A combination of cellulose fibrils glued together by lignin and hemicellulose known as biofibers and snail shells at nanoparticle sizes is investigated in this study. The main components of natural fibers are lignin, cellulose, hemicellulose, waxes, and pectin [75-77]. As shown in Figure 2.4, the microstructure of natural fiber encompasses different hierarchical structures, and this single fiber has a diameter of about 10-20 µm, comprises four concentric layers, including primary, outer secondary, middle secondary, and inner secondary walls.

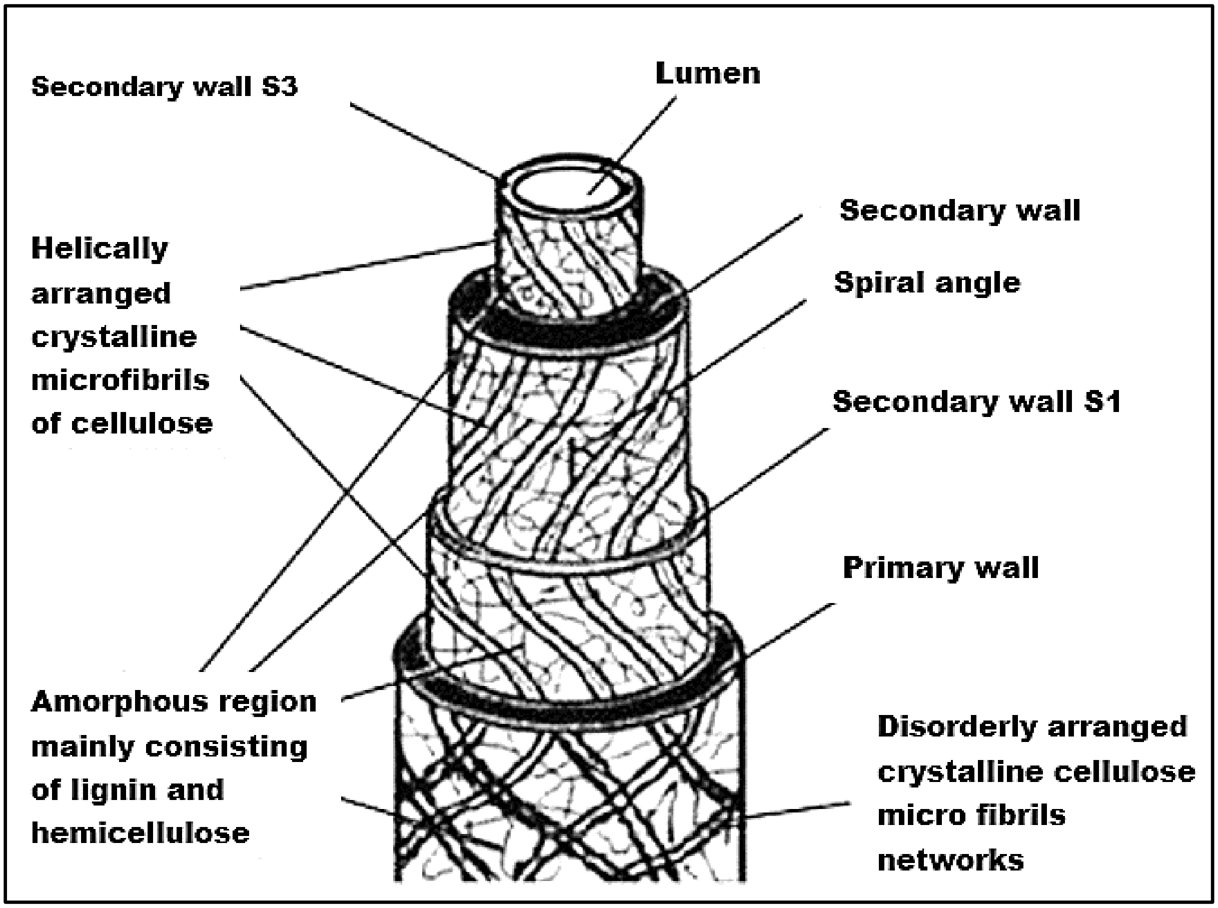

Figure 2.4: Structural component of a biofibre [78, 79]

Lignin is a naturally prevailing sweet-smelling polymer found in most land-dwelling plants at approximately 15 to 40% dry weight. It is the main element of vascular plants and polysaccharides in nature [80]. Lignins often play significant roles in forming the projectile of cell walls, particularly in bark and wood, because of rigidity transfers. The lignin structure is exceptionally complex as monolignols are linked through several connections into a three-dimensional network. It has constituents of a very high molecular mass of copolymer of aromatic and aliphatic. Pectin, functioning as a binder to hold fiber together, exhibiting a polysaccharide nature like cellulose and hemicellulose [79, 81]. Chemically, lignin is a cross-linked phenolic polymer with stable thermal behavior [80, 82]. The chemical complexity of this polymer provides woody plants and trees structural integrity.

Furthermore, the distribution of lignin between hemicellulose and cellulose provides binding and stiffening of plant fibers that may be related to the mechanical strength exhibited by plant fiber. Ragauskas et al. [83] confirmed that most large-scale industrial procedures use plant polysaccharides by burning lignin to produce the necessary power to convert biomass efficiently.

Cellulose is the essential constituent of rigid cell walls that border plant cells create plant leaves, stems, and branches more durable. As the most substantial skeletal component, it possesses inexhaustible polymeric raw material with magnetic structure and properties. This structure made cellulose regarded as the most abundant natural polymer found in the plant, some bacterial and green algae. Cellulose is a linear sequence of ringed glucose with a flat ribbon-like conformation. Cellulose is a green polymeric material containing 1,4-β-D- anhydroglucose (C6H11O5) reiterating units merged by 1,4-β-D-glycosidic connections at C1 and C4 position, and every single unit includes three different hydroxyl collections as shown in Figure 2.5 [79, 84, 85].

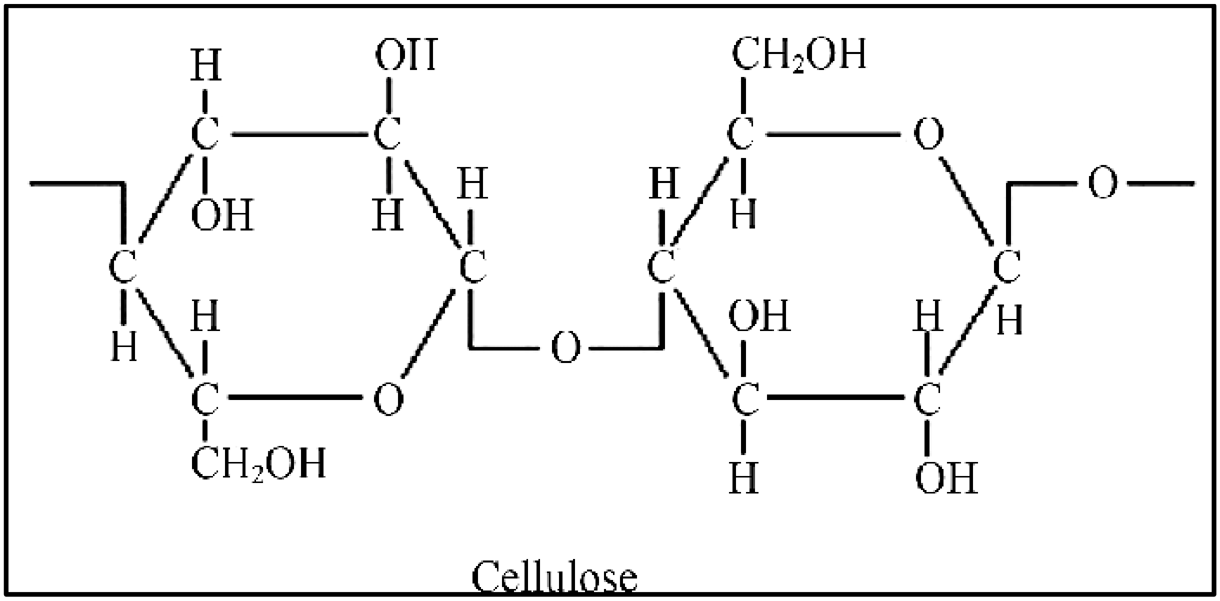

Figure 2.5: Schematic diagram of the cellulose structure [86].

It possesses a desirable high molecular weight with a polymer that can be defined as renewable, biodegradable, and natural. Furthermore, cellulose possesses high specific strength and stiffness, and biodegradability is a looked-for fiber ratio readily available from the natural source. The discovery and knowledge of cellulose chemistry and structure have led to several innovative techniques and materials [87]. However, natural fiber has drawbacks that include but are not limited to water absorption, interfacial bonding, and material degradation. Therefore, the following section discussed how these drawbacks affect natural fiber in the composite.

2.5.2. Challenges of natural fibers usage in composite applications

Despite the enormous advantages of natural fiber, they still face low modulus, disintegration in alkaline, a biological attack, high moisture absorption, and unevenness in physical and mechanical properties compared with standard engineered material or synthetic fibers [79, 88]. Furthermore, Ho et al. [88]

confirmed that poor wettability reduces adhesion and degradation at the fiber/matrix interface. These deteriorate fiber during the manufacturing processes, which are the main courses of biocomposite failure. Similarly, a review conducted by Pickering et al. [89] stated that one of the main factors affecting the mechanical performance of natural fiber includes but is not limited to fiber selection. This selection includes types, harvested time, extraction method, aspect ratio, fiber treatment, fiber content, and orientation. These factors make selecting quality fiber a challenge. Nevertheless, the banana is a perennial plant that replaces itself.

Besides, bananas do not grow from a seed but a bulb or rhizome, and it takes 9 to 12 months from sowing a banana bulb to harvesting the fruit. Therefore it is well available [90]. Furthermore, Banana fiber, known as lignocellulosic fiber obtained from the banana plant's pseudostem (Musa sepientum), is a bast fiber with relatively good mechanical properties. Consequently, numerous studies have suggested that banana fiber is a suitable reinforcement for improving composite materials' mechanical strength [91-94]. The characteristics above of natural fiber often lead to fiber-matrix compatibility reduction, affecting surface bonding and compromising the overall composite's performance. Because of these limitations, this study constrains the application of natural fiber biocomposite to train and automobile vehicles' internal mechanisms.

2.5.2.1 Moisture absorption in fibers

Natural fiber's moisture immersion rate has been identified as one factor that reduces the plant fiber-filled biocomposite mechanical strength [6, 95-97]. This discovery led to a rigorous investigation on mitigating the water intakes and increasing the natural fiber and matrix's interfacial bonding to improve mechanical properties [98-102]. Van de et al. [102] enhanced the adhesion and interfacial bonding of UD flax fiber-filled composite using an alkaline fiber chemical treatment after weak interfacing bonding of UD flax fiber was identified. Results show that the treated fiber exhibited a higher mechanical property compared to non-treated.

Similarly, Anbukarasi and Kalaiselvam [103] experimentally investigated the influence of fiber volume loading (0.3–0.5V_f), dimension, and chemical treatment of fibers on mechanical, thermal, and water absorption behavior of luffa reinforced epoxy composites. The naturally available luffa fiber mat shapes were fabricated in three different mediums: short fibers and mat-shaped fibers were processed and used to develop fiber reinforced epoxy composite. Results gathered from this study showed that 0.4 V_f *treated mat fiber-reinforced composite* exhibited higher tensile, flexural, and compressive impacted the strength of 13.7%, 6%, 72.43%, and 163.6%, respectively, than untreated fiber-reinforced composites.

The improvement in mechanical properties observed was related to the homogeneous dispersion of fibers in epoxy polymer and good interfacial bonding. These two studies show that if a reinforcement does no merged with the matrix, it does not add any value in terms of strength improvement. Subsequently, fiber treatment was adopted to acquire efficient hydrophobic hurdles and required interfacial bonding with the matrix that enhances the bond of biofiber and polymeric material. According to Li et al. [104], fiber's chemical treatment helps improve the adhesion between the fiber surface and the polymer matrix. Undertaking this may not only modify the fiber surface but also increase fiber strength. Therefore, the following section discussed different chemical treatments giving to biofiber.

2.5.2.2 Fibre treatment

The mechanical strength improvement for natural fiber-filled composite depends on the interaction and bonding force acting between the reinforcement and matrix. This fact has inspired researchers to consider several steps for enhancing fiber and matrix surface bonding ability. Among numerous techniques that have been implemented in the past, giving chemical treatment has been one of the most effective ways of improving the fibers' surface property (reinforcement) [105-113]. Ho et al. [88] argued that natural fiber-filled polymer composite properties are principally ruled by the pre-treatment of fiber and the manufacturing process adopted for composite fabrication. Given this, different chemical treatment has been suggested; these include but not limited to alkali, silane, and acetic anhydride treatments; however, alkali treatment is commonly used.

Each of these chemical treatments has different effects on the reinforcement, which often influences mechanical properties. According to Sunija et al. [114], silane treatment is a giving chemical treatment for improving the surface property of reinforcement, enhancing the mechanical strength of natural fiber-based composite [115]. Similarly, Haque et al. [116] confirmed that acetic anhydride treatment is one way of enhancing the surface bonding capacity of natural fiber-matrix in a composite as improvement in thermal and mechanical properties was achieved using this technique.

Among several chemical treatments suggested from scientists' steps, alkali-treated fiber using sodium hydroxide solution has been identified to be the most effective. The investigation results stated that giving alkali treatment to natural fiber enhances the fiber and matrix's surface adhesion ability. [109, 113]. Goda et al. [105] studied the influence of load application through natural fiber's mercerization using ramie fibers as a case study. This load technique application was employed to improve the mechanical properties of the fiber. Before this investigation, fibers were alkali-treated by 15% of sodium hydroxide (NaOH) solution and was subjected to a load of 0.049 N and 0.098 N afterward.

The results reported that chemical treatment improved fiber tensile strength up to 18%, and fracture strain drastically increased from 0.045 to 0.072 compared to untreated fiber. A notable decrease in the Young modulus of treated fiber was also observed. The improvement in strength and fracture strain upon mercerization was related to change in morphological and chemical structures in microfibrils of the fiber. Furthermore, Meon et al. and Edeerozey et al. [106, 107] soaked kenaf fiber with 3%, 6%, and 9% sodium hydroxide (NaOH) solution to investigate the optimum concentration chemical required for fiber treatment. The fiber was soaked for a day and dried for 24 hours before testing. They discovered a significant improvement in treated fiber's mechanical properties at an optimum level of 6% compared to untreated and another sample treated with 3% and 9% NaOH.

Similarly, Paul et al. investigated the effect of fiber loading and chemical treatment on the banana fiber-filled composite's thermophysical properties. An alkaline chemical treatment was given to banana fiber using 2% and 10% sodium hydroxide (NaOH) solution. The experimental results show that 10% of sodium hydroxide treated banana fiber composite exhibited superior thermophysical properties than 2% NaOH treated banana fiber composite. This result suggested that chemical properties positively affect natural fiber, and it shall be adopted in this present study.

2.5.3 Properties of natural fibers

Natural plant fibers possess specific high mechanical strength and stiffness; however, lower than synthetic fiber [103]. Table 2.1 clearly shows that natural fiber has comparable properties such as elongation at Break, stiffness, and density compared to synthetic fiber. These mechanical properties can be modified for different applications by selecting suitable fibers, matrices, additives, and fabrication methods.

Table 2.1: Comparison of mechanical properties for synthetic and natural reinforcing fiber [89, 91, 117-120].

Fiber	**Tensile Strength (MPa)**	**Young's Modulus (GPa)**	**Elongation at Break (%)**	**Density (g/cm^3)**
Synthetic				
E-Glass	2000 – 3500	70	2.5	2.5 – 2.59
Aramid	3000 – 3150	63.0 - 67.0	3.3-3.7	1.4
Carbon	4000	230.0 – 240.0	1.4 – 1.8	1.4
Natural				
Bamboo	140 – 800	11 – 32	2.5 – 3.7	0.6-1.1
Banana	529-914	27-32	3	1.31-1.33

Jute	200 – 800	8 – 78	1.5 – 1.8	1.3-1.49
Kenaf	223 – 930	14.5 – 53	1.5-2.7	1.4
Flax	345 – 2000	27.6 – 103	1.2 – 3.3	1.4-1.5
Sisal	365 – 700	9.0 – 38	2.0 – 7.0	1.33-1.5
Hemp	270 – 900	23.5 – 90	1.0 – 3.5	1.4-1.5
Coir	95 – 230	2.8 – 6	15 – 51.4	1.15-1.46
Ramie	1.0 – 1.55	400 – 1000	24.5 – 128	1.0-1.55

Consequently, this provides fibrous material suitable as a replacement or to serve as an alternative to synthetic fiber [88]. Significantly, Banana fiber exhibit a comparable stiffness, elongation at Break, and density with E-glass fiber shown in Table 2.1 and confirmed its suitable replacement. Moreover, a modified or treated plant fiber with coupling agents often have functional linkage with the matrix, which eventually improves composite mechanical strength [121]. Plant fiber's core importance is low cost and density, combined with a renewable matrix to produce a biobased (greener) and lightweight composite with improved strength and stiffness [121-123].

2.5.4 Banana fibers

Bananas are one of the world's most luscious fruit. It is cultivated and consumed in over 150 countries, with over 105 million tonnes of fruit produced annually. Asia and America are leading producers of bananas, accounting for 57% and 26% of total annual production, respectively, and Ecuador is the largest exporter of banana fruits globally. [124-126]. Bananas are said to be native to tropical South and Southeast Asia. They are among the most important commercial subtropical fruits grown in South Africa. Besides, they are planted for sale in local markets or self-consumption, and a small fraction of banana produced in South Africa is exported to the global market.

Bananas are produced mainly in Mpumalanga, Limpopo, and the North and South Coasts of Kwazulu Natal [127]. Over 450,000 tons of banana were produced in South Africa in the year 2013/14, and Kwazulu Natal has the central growing area of accounting for 15% (1700 Ha) of the total banana plantation area.

Figure 2.6: Banana (A) mature plant and (B) Erected fiber.

Moreover, these banana fruits are produced by several pieces of large herbaceous flowering plants in the genus *Musa* that grows in clusters hanging from the top of the plant. Significantly. This plant's pseudostem can bear one bunch in its life, leaving behind many agricultural residues (starchy and lignocellulosic biomass) [128]. There are records for banana fruit consumption globally, but there is no record for using the agricultural residue. After harvesting the fruit by cutting down the tree, the banana plant stem (pseudostem) dies and produces a large number of agricultural residues that cause environmental pollution [129] [130].

Researchers have implemented different techniques of extracting valuable additives such as fiber, cellulose, and lignin from agricultural residues to increase the importance of banana plantations. These additives are extracted using different techniques, including but not limited to chemical, mechanical, or biological methods. The extraction of banana fiber using biological retting, which yields more fiber bundles without causing harm to the environment, has commonly been reported in many studies [131-134]. The typical mature banana plants and the banana fibers extracted from the plant stem using the biological procedure are shown in Figure 2.6. This fiber has found use in packing cloth, string, ship towing ropes, cordage, and wood-pulp paper making.

Moreover, naturally sourced fiber has several advantages over synthetic fibers, such as renewability, appropriate stiffness, low density, mechanical properties, and high disposable. These advantages attract exploration into the development of composite and biocomposite. However, achieving improvement in banana fiber-filled composite properties depends on the fiber length and content incorporated. Therefore, the following section discusses the effect of distance and content of banana fiber on composite or biocomposite.

2.5.5 The effect of length and content of banana fiber on composite

The lignocellulosic fiber extracted from banana pseudostem has proved beneficial reinforcement in thermoplastic and thermoset matrices [92, 135, 136]. They are commonly used as chopped strands incorporated to enhance the strength of polymeric materials. The critical length and fiber contents are essential factors in determining the load-bearing capacity of composite.

According to Mohan and kanny, fiber will not effectively bear the composite load when the fiber length incorporated is lesser or greater than a critical length [137]. Based on this fact, they studied the effect of fiber critical length on the mechanical properties of composite material. Composite was prepared with fiber loading ranging from 30% fiber loading and fiber length ranging from 30mm to 45mm. It was observed that composite filled with a fiber length of 35mm offered better properties, although the fiber was infused with nanoclay. Paul et al. [79] also synthesized and characterized a biocomposite derived from the banana plant stem. The biocomposites were prepared with fiber loading ranging from 20% to 50%. The results showed that improved mechanical and thermal properties were at 30% loading.

Moreover, Boopalani et al. and Pothani et al. [138-140] argued that improving chopped banana-reinforced composite properties solely depend on the fiber critical length and volume of loading. In this regard, Laly et al.[141], investigated the effect of fiber length and content on the mechanical properties of short banana fiber reinforced polyester composite. It was discovered that superior tensile strength was observed at 30 mm fiber length, while impact strength gave the maximum value for 40 mm fiber length. Similarly, 40% loading of fiber exhibited higher mechanical properties. Based on the information provided above, it could be concluded that the loading of banana fiber with a length range from 30mm and 40mm at 40% loading is an effective way of enhancing composite mechanical properties.

2.6 FILLERS

Fillers, both organic or inorganic, play significant roles in improving polymeric material characteristics [142-145]. They may be incorporated to increase strength, conductivity, and thermal stability, or resistance to indentation. Dittanet and Pearson [146] argued that filler or fillers are used to improve thermal, physical, and chemical and improve bonding systems of composite favorable for enhancing mechanical properties. Loading of this filler may improve one property and negatively affect another in some cases. They are often used to reduce the cost of expensive polymetric matrix and binders, which eventually reduces production cost [31, 33, 147-149]. Several filters have been employed to serve as reinforcement in polymer composites. Despite several fillers identified with potential for composite reinforcement, SiO_2, TiO_2, and carbon-based fillers such as carbon nanotubes and graphite nanopowder, calcium carbonate ($CaCO_3$) found most suitable and commonly used [149-153].

As mentioned earlier, fillers with a high concentration of calcium carbonate (CaCO3) are extensively used due to their accessibility, good mechanical strength, thermal stability, and biodegradability [154]. This discovery led to a rigorous investigation of calcium carbonate-based filler, and consequently, montmorillonite and kaolinite, referred to as nanoclay, were found to be most suitable [155, 156]. Studies conducted confirmed the effectiveness of nanoclay in improving several composite properties [142, 157]. However, it has been discovered that the end-life of nanoclays has adverse effects on human health and, at times, expensive compared to naturally sourced fillers [145]. This fact consequently reduced the usage of this filler—besides, Marrot et al.[158], claimed that the negative impact of synthetic thermoset polymer and fiber on the environment could be reduced in two ways, first, by replacing synthetic fiber with natural fibers. And secondly, by replacing the petrochemical component in the matrix with biobased renewable equivalents. This clue rigorously increases studies towards the development of green composite using biobased ingredients.

Composite materials, especially biodegradable composites from bio-fibers, bio-fillers, and bio-polymers, are reasonably fit into this global sustainability shift. These biodegradable materials extracted from renewable sources such as agricultural waste and forestry feedstocks, including wood, agricultural waste, grasses, and natural plant fibers, have been used for numerous materials for durable goods application. This awareness inspired a scientist to source a natural constituent that meets societal needs and supports global sustainability. Subsequently, in recent decades, natural fillers extracted from wood, hair, and animal shell have been investigated to enhance thermal stability, degradation, strength, and physical properties of polymeric materials [42]. The search for this suitable material led to the discovery of eggshells.

Eggshell was identified as a potential filler due to the higher calcium carbonate content (~95% $CaCO_3$) in this material [159-161], which was eventually used as an alternative to commercial $CaCO_3$ mentioned above. Research has been done on mollusk shells, animal bones, and eggshell materials that have been investigated for $CaCO_3$, and it was proved that these materials have adequate filler characteristics for different applications [42, 162]. In this regard, the African giant snail is selected as a reinforced filler, hoping to have sufficient CaCO3 providing excellent inter-linking property, improving mechanical strength and moisture absorption properties. Several studies have demonstrated that these biological materials, in microparticle size, form polymeric materials, resulting in improved composite materials. A combination of these naturally sourced materials has been developed to produce advanced materials with desired properties [42, 72, 163]. However, there is scarce information on the materials' fundamental properties that could be exploited for bio-composites development. This issue may be due to the size of the biological materials -

shells, in particular, it does not have adequate size/space required to produce a standard specimen for the measurement of mechanical properties. Therefore, these shells are milled to micro/nanoparticles and disperse in materials to develop composite. Different milling techniques are used for small organic particle synthesis, and the subsequence section provides information in this regard.

2.6.1 Milling procedure for micro and nanoparticle manufacturing

Nano-sized calcium carbonate ($CaCO_3$) has received special consideration for several applications due to its availability, good mechanical strength, and thermal stability [154]. It is commonly used as filler or reinforcement for polymeric materials, papers, and paints. This carbon-based material has been obtained from several resources such as rock, human, and animal waste. Over many decades, montmorillonite and kaolinite with a high concentration of $CaCO_3$ are sourced and synthesized using different techniques. These fillers are sourced from rock and manufactured using either gas pressure blasting or explosion method [155, 156, 164]. However, these fillers' harmful impacts and climate change factors have compelled material scientists to source filler material from natural resources. And the filler material should offer suitable filler material properties and meet societal needs and support global sustainability.

Consequently, in recent decades, calcium carbonate ($CaCO_3$) of different particle sizes extracted from natural resources such as bones, horns, and animal shells are used as reinforcement to enhance thermal stability, degradation, strength, and physical properties of polymeric materials [42]. Several research studies have investigated the functional group, elemental composition, and minerals present in eggshells, mollusk shells, and animal bones [42, 162, 165, 166]. These natural resources were discovered to have a higher calcium carbonate content ($CaCO_3$), especially eggshell, which was confirmed to have about 95% $CaCO_3$ [159-161].

Furthermore, mollusk shells, oyster shells, and animal bones have been investigated for $CaCO_{3,}$ and they were found to have adequate filler appropriateness properties for different applications. Consequently, calcium carbonate produced from animal waste has been suggested to be an alternative to commercial $CaCO_3$ for some applications, including dental and medical applications [42, 162, 167-170]. However, there is limited literature where $CaCO_3$ synthesized from these natural resources is used either as a filler material to fabricate composite or polymer material reinforcement. The limited research may be because milling a large quantity of these materials to smaller particle sizes comes with many challenges, including but not limited to particle agglomeration.

Despite the availability of numerous milling techniques used for small organic particle synthesis, mechanochemical technology has been found to be the most effective [164, 171]. This biological synthesis mechanism has been regarded as a significant revolution towards achieving a sustainable and efficient process of producing small molecular sizes of grains [172]. Numerous researchers confirmed that mechanochemical techniques are a branch of chemistry that covers any chemical transformations induced mechanically or physio-chemical changes of the material of any state of combination due to the influence of mechanical energy such as friction, compression, or shear [167, 173-176]. A mechanochemical procedure such as hand grinding or ball-milling has been reported to influence materials' structure and composition. This innovation brings about an opportunity to prepare and fabricate nanomaterials particles using a top-down tactic [177].

The efficient procedure of producing small molecular sizes of grain achieved using mechanochemical technique has made it a promising candidate for solvent-free synthesis. [171, 178, 179]. However, solvent-free synthesis may not apply to all materials, especially calcium carbonate-based materials, where particles' agglomeration is dominant. Researches have proved that the dry milling technique causes a large agglomeration of the particle during synthesis. This structure often results in bimodal size distribution, weakening the nanocomposite bond [180-183].

2.6.2 Snail shell

Snail shells are regarded as a discarded bio-shell waste of snail remnants from seashore, restaurants, dermatology, and snail sellers. Shell is an outer skeleton or exoskeleton, which serves not only as crucial protection against the sun, against drying out and predators for both lands, intertidal marine and freshwater snail [184, 185]. In particular, gastropod shell has constituted a severe threat to the environment with little or no economic value as they are arbitrarily abandoned after consuming the inner edible meat [185]. Barros et al. [186] confirmed that over 80,000 tons of mussel shells alone are disposed of as waste annually.

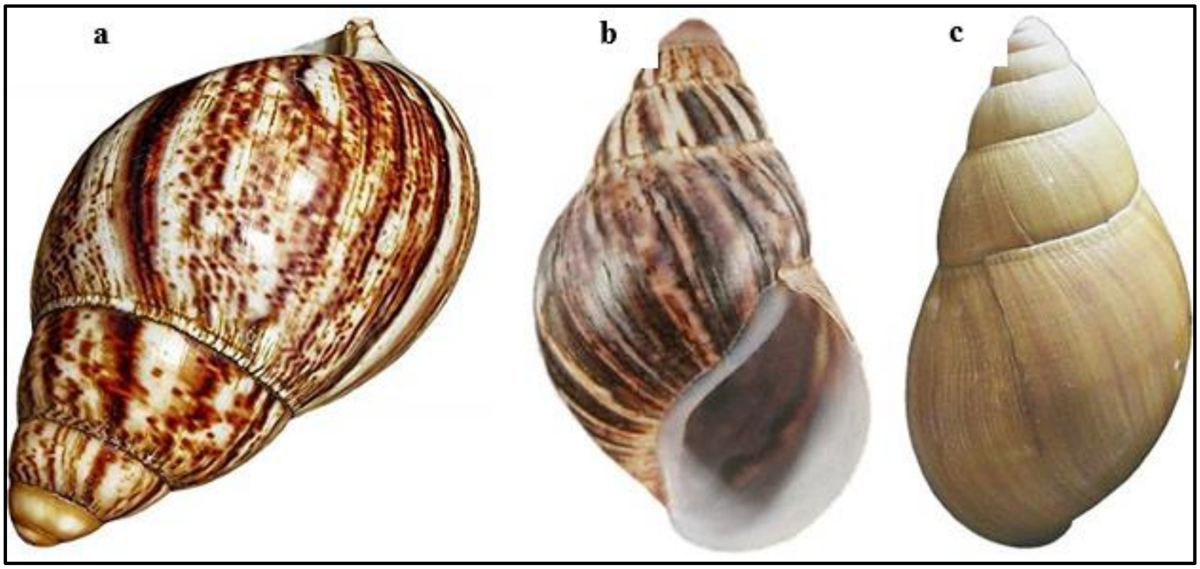

Figure 2.7: Snail shell (a) Achatina Fulica (Giant Africa land snail), (b) Achatina Achatina, (c) Achatina Marginata

Land snail shells are wasted in billions of tons every year. In particular, in West African countries such as Nigeria, Ghana, Cote d'Ivoire, snail meat is famous for consumption. In Cote d'Ivoire, over 7.9 million tons of snail meat are eaten annually. However, Ghana and Nigeria's demand currently overtook snail meat supply, and the shells become a waste [187]. Denene Erasmus reported strong demand for snails globally, particularly in France, Spain, Italy; however, France is the highest snail-consuming among these countries. Typically, a French person can eat up to 1kg of snail in a year, and the country is consuming around 50,000 tons annually. Spain consumes roughly 14,000 tons depending on the import to match internal demand [188].

Consequently, snail farmers rear different land snail species to meet local and foreign markets. The snail species include *Achatina Fulica* (Giant Africa land snail), *Achatina Achatina*, and *Achatina Marginata,* as shown in Figure. The main difference of this snail is size, as *Achatina Fulica* is the biggest. Additionally, many commercial farms of land snail have been identified at Gauteng, cape town, South Africa, where tons of snail are reared to meet the demand of sail meat [24, 25].

Even though a tremendous amount of snail is produced yearly, the IOL news reported a shortage of 40-48 000 tons of snails for the international market. This need led to the opening of the first South African snail farm Western Cape [25]. This report only discussed the meat, but nothing has been said about the shell because they are regarded as unwanted. Despite considerable foreign and local demand for snail meats, commercial snail farms that operate in foreign countries like Europe and the United States hardly exist in Africa [187]. This fact implies that tons of snail shells are wasted in those countries as well. Land snail shells' availability is guaranteed globally and proves that this research's expected output is sustainable. Additionally, the shell usage regarded as waste presents a significant contribution to advancing the economic importance of snail rearing farms.

Aside from the availability of shells, research has shown that both freshwater and land snail shells have a high content of $CaCO_3$, and the loading of shells at different particle sizes confirm as an effective way of improving some properties of polymer materials [42, 162]. In this regard, Nwanenyi et al. [72] conducted an investigation on the effect of loading periwinkle shell at different particle sizes (75µm, 125µm, and 150µm); filler content (0 to 30 wt%.), and compatibilizer (0.5 to 2.5 wt%) on mechanical properties of polyethylene. The mechanical properties explored on the shell particles and compatibilizer-filled polyethylene include but are not limited to tensile strength, elongation at break, tensile modulus, flexural strength, impact strength, and hardness. According to the experimental results, an improvement in mechanical properties with a corresponding increase in filler loading was observed.

However, many of the land shells are underutilized, and less or no research work has been done to investigate their basic properties. In this present study, the fundamental properties of *Achatina Fulica* shells were investigated before used as nanofiller. It is well known that filler and reinforcement are not complete without polymer, which serves as a binder in the composite. Therefore, the following section discussed the matrix for biocomposite.

2.7 MATRICES IN BIOCOMPOSITES

Biocomposite may combine natural fibers and synthetic binders or greener resin systems, thermosetting and thermoplastic polymers [79]. The present study is narrowed to biobased thermosets polymer and modified by loading nano calcium carbonate and banana fiber.

2.7.1 Thermoset

Thermoset can be referred to as an irreversible polymer hardened by a curing agent. This process is achieved by mixing a soft solid or viscous liquid prepolymer with a catalytic or hardener. Besides, thermoset liquid at room temperature allows easy loading of filler or fiber before adding the catalyst that makes it cured or hardened. This mixing process often results in chemical reactions that create widespread cross-linking between polymer chains to create an infusible and insoluble network.

Most of the thermosetting polymer used in the composite industries is produced from petrochemical products. Nevertheless, the growing demand for eco-friendly plastics increases bio-based polymer usage for composite production [189, 190]. Several bio-based polymers, such are cellulose plastics, polylactic acid, vegetable oil, and polyhydroxy alkonate, have been extensively developed and commercialized [191, 192]. However, they are thermoplastic polymers.

In recent decades, several biobased thermoset polymers such as epoxy resin have been developed with some percentages of extracts from plants, linseed, soybean, Jatropha, and vegetable oil used to fabricate biocomposite. This biobased resin is modified by either synthetic or naturally sourced fiber and fillers to fabricate green composite [192, 193]. Sandeep et al. [194] studied the mechanical behavior of green composite made by incorporating agro-residues as soy stalk (SS), corn straw (CS), and wheat straw (WS) into the bacterial polyester poly(3-hydroxybutyrate-co-3-hydroxyvalerate). The effect of biomass fibers on the mechanical, thermal, and dynamic mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) was investigated. The loading of these biomass fibers significantly increased according to the result reported in this study.

2.8 SUMMARY

The review conducted was on biocomposite from different sources, including natural fibers and agricultural waste. It shows that natural fiber is becoming a material choice for various industries, including mass transit, automobile, and aerospace. It also clear that despite extensive research conducted on the discovery of natural materials for different applications, there still some natural materials that needed to be sourced and investigated.

Although several kinds of research have been done on snails, limited information is available on their shells' mechanical strength and how this can improve composite properties at nano-scales. Additionally, the reinforcement potential of banana fiber in the composite or hybrid composite systems is reviewed from different studies. However, it has been found that there is no literature available on the development and characterization of nano-$caco_3$ synthesized from *Achatina Fulica* snail shell and banana fiber reinforced biocomposite.

The idea of using wasted snail shells synthesized to nano- $caco_3$ through mechanochemical techniques has been suggested. This technique is to be used as a nanofiller in banana fiber-filled green matrix hybrid composite formation. Combining these materials from natural sources led to the development of biocomposite with comparable mechanical properties that could be used for non-functional motor vehicle components.

2.9 RESEARCH OUTPUT

Gbadeyan O.J, S. Adali, G. Bright, and B. Sithole, "Nanofiller/Natural fiber filled polymer hybrid composite: A review," *International Journal of Engineering science and Technology Review. Under review. (Manuscript number: 3832)*

CHAPTER THREE: PHYSICAL AND MORPHOLOGICAL PROPERTIES OF SNAIL (*ACHATINA FULICA*) SHELLS FOR BENEFICIATION INTO BIOCOMPOSITE MATERIALS

Author contribution:

Gbadeyan O.J *conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript*

Prof. S. Adali, Prof. G. Bright, and Prof. B. Sithole *provided material and equipment used for experimenting, supervised all process, and proofread the manuscript*

3.1 OVERVIEW

In this chapter, information on microhardness and flow strength (tensile) of a shell of an African Giant snail (*Achatina Fulica*) was measured as a function of indentation load. It reveals the resistance of the shell to indention and external pulling force to determine its suitability for biofillers for polymer reinforcement application. It also provides information on the influence of loading direction on the hardness of the nacreous (inner layer) and prismatic (outer layer) structure of the shell to determine the hardness variance on both layers. The Microhardness measured on the nacreous and prismatic structures of the shell was also provided. The morphology of the shell surface showing an interlocking 0structure with a large surface for binding to the organic matrix was analyze. This chapter suggested that *Achatina Fulica* shells can be beneficiated into filler that may improve the mechanical properties of polymeric composite materials due to their improved hardness and strength.

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Physical and Morphological Properties of Snail (*Achatina Fulica*) Shells for Beneficiation into Biocomposite Materials

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Abstract

In this study, microhardness and flow strength (tensile) of a shell of an African Giant snail (*Achatina Fulica*) were studied as a function of indentation load. The influence of loading direction on the hardness of the nacreous and prismatic structure of the shell material was analyzed. The results revealed that microhardness measured on the shell was dependent on the load on the nacreous and prismatic structures. Indentation loading between 50 and 500 kN induced tensile strengths that ranged between 675–1050 and 390–810 MPa on the prismatic and nacreous layers, respectively. In addition, the morphology of the shell surface exhibited an interlocking structure with a large surface for binding to the organic matrix. The observed reinforcement of the shell explained the hardness property of the shell. The improved hardness of the shell implies that it can be beneficiated into filler that may be used to improve the mechanical properties of polymeric composite materials.

Keywords Snail shell · Microhardness · Tensile strength · Indentation loading · Microstructure

1 Introduction

Snail shells are a ubiquitous waste in the environment. Many of them are generated after the processing and consumption of snails, e.g., by snail merchants, food, and cosmetics industries [1]. Accumulation of waste shells in the environment constitutes a serious threat to human health and sometimes causes blockage of waterways [2, 3]. A study by Arias and Fernández [4] on shells, bone, and teeth classified them as ceramic biocomposites consisting of layered assemblies of microscopic amounts of macromolecules with well-ordered inorganic structures rich in calcium that provides a material with unique morphologies and properties. Microstructural features such as organized, layered organic/inorganic assemblies and the existence of spongy and fibrous elements in many biological components have become an inspiration for the development of biocomposite materials.

Furthermore, the existence of organic and inorganic structural networks at molecular and micro-levels often form synergistic effects that significantly improve the mechanical properties of advanced nano-laminates and other composite materials made from them [5, 6]. Several studies have demonstrated the addition of these biological materials, in microparticle size form, to polymeric materials and this resulted in improved composite materials. Also, a combination of two or more of these naturally sourced materials has been developed to produce advance materials with desired properties [7–9]. However, there is a dearth of information on the fundamental properties of the materials that can be exploited for the manufacture of biocomposites. This may be due to the size of the biological materials—shells, in particular, do not have adequate size/space required to produce a standard specimen for measurement of mechanical properties.

Despite this, valuable information on mechanical responses of the shell, such as tensile, may be obtained by conducting nano and micro-indentation (Vickers hardness test) studies on shell samples. Material hardness may not always be a fundamental property of a material; however, mechanical properties such as yield strength, work hardening, and true tensile strength of a material may be

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determined through nano and micro-indentations on the material under loading conditions.

Furthermore, material hardness is directly linked to numerous properties including resistance to plastic deformation, resistance to scratch, indentation, deformation, friction, wear, and abrasion [10, 11]. Correlation connection between hardness and tensile strength usually depends on the microstructure of the material [12, 13], and resistance to deformation depends on its modulus of elasticity [14, 15]. Vickers hardness testing technique is widely used to determine the resistance to indentation of ceramic materials but has not been reported for biological or inorganic composites such as *Achatina Fulica* snail shells although nano-indentation of the shell structure on a micro-scale has been reported [16–18]. In this regard, this study provides information on microhardness, and its correlation to tensile strength, for *Achatina Fulica* snail shells. *Achatina Fulica* or African land snail is one of the largest species of snails in the world and can grow up to 20 cm. The snail is widely consumed in Africa; hence, the snail shells are widely available.

2 Experimental Details

2.1 Materials and Method

Shells of the *Achatina fulica* snail were collected from the University of KwaZulu-Natal, Westville campus soccer pitch. They were washed in a soap solution, rinsed with running tap water to remove dirt, and then dried under room conditions for 7 days before testing.

Procedures used in testing of ceramic materials were used to prepare cross-sections of shell samples for testing. This involved cold casting in resin at room temperature, polishing by using silicon carbide particles, and lubrication. Relatively flat shell specimens were cold cast under 29 KN force, baked for 12 min at 50 °C and then cooled for 3 min. Hardness indentations were performed on casted specimens particularly on the outer and the inner surfaces of the shell. Vickers hardness tests commonly used for determining microhardness of ceramics or single crystal materials were adopted for this study (ASTM A370). This hardness testing technique is typically a load-dependent procedure with a corresponding increase in applied load [19–21]. Microhardness values of the shell were determined as a function of the indentation load at the cross-sectional area of both the inner and outer layers of the shell. To ensure stable mounting, the shell samples were cut using a saw blade and shaped with a file to 25 mm by 10 mm dimensions.

Vickers hardness measurements were conducted using a Leco (model M-400-H) Vickers hardness tester. The hardness was measured at different indentation loads of 50 N, 100 N, 200 N, 300 N, and 500 N at 15 s loading durations. Ten indentations values were randomly taken for each load on all the specimens, and the mean values taken were reported. Microhardness values were converted to tensile strength using the ceramic hardness unit's commonly used conversion table (11).

Microstructural studies were conducted on a ZEISS EVO LS 15 scanning electron microscope (SEM) to examine the structural formation of the shell.

3 Results and Discussions

3.1 Morphological Structure of *Achatina Fulica* Shell

The microstructure of broken-off piece *Achatina Fulica* shell was examined using a scanning electron microscope at 99X magnifications to ascertain the route of its hardness property. A typical SEM image is shown in Fig. 1.

The examination indicated that the shell was composed of a unique structure, which may possibly be classified as crossed-lamellar, which served as inner reinforcement

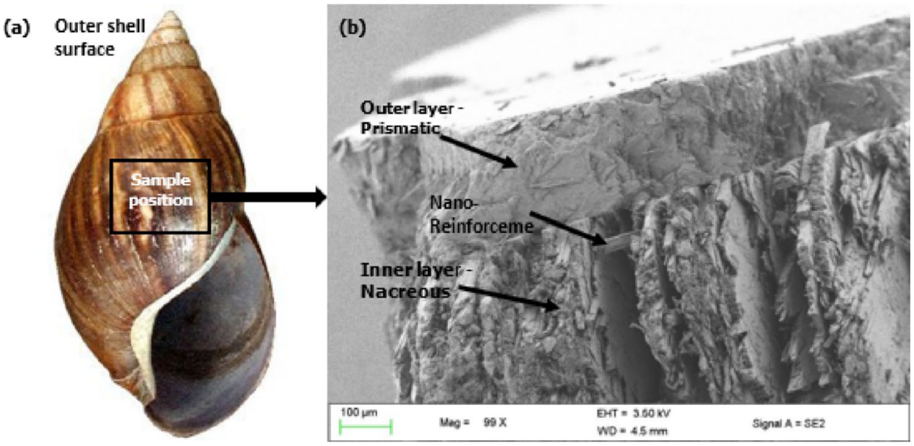


Fig. 1 Image **a** view of the outer section of the *Achatina Fulica* shell and the position where a sample was cut and **b** SEM image of the cross-section of the removed piece cross-sectional surface (99 magnification)

supporting the uppermost layer (prismatic layer), and homogenously foliated with the nacreous (inner layer) as shown in Fig. 1b. This confirmed that the snail shell had a distinctive structure comprised of biological tissue components with numerous linkages and distribution of soft and hard components. This is consistent with a study conducted by Tomislav et al. [21], who reported on the microstructure of mollusk seashell.

The Interlocking of the biological component with a relatively smooth surface was observed on the prismatic layer. The smooth surface could be a result of polishing done on the cut shell sample. A layer of aragonite platelet that could be referred to as reinforcement was also observed in the inner layer of the shell. This cross-sectional structure formation is advantageous for external force resistance. Figures 2 and 3 indicate that this structure is the main functional mechanism for high resistance to indentation, resulting in relatively high microhardness and tensile strength properties shown in the figures.

3.2 Hardness Property

The relationships between the microhardness of the outer and inner shell surfaces structure with different indentation loads are shown in Fig. 2.

As expected, the outer structure (prismatic layer) showed better resistance to indentation than the inner structure (nacreous layer) irrespective of the applied force. However,

Fig. 2 Graph showing the relationship between microhardness and the applied load

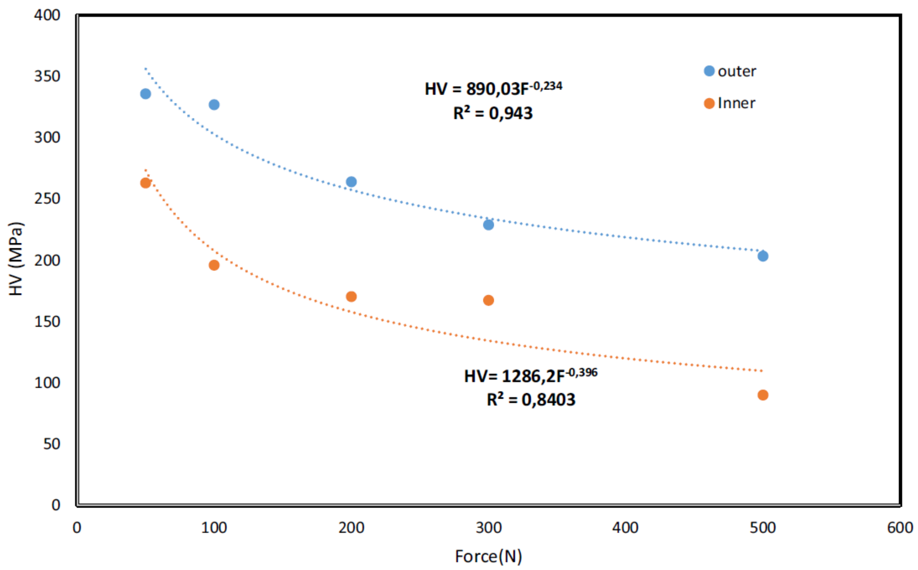
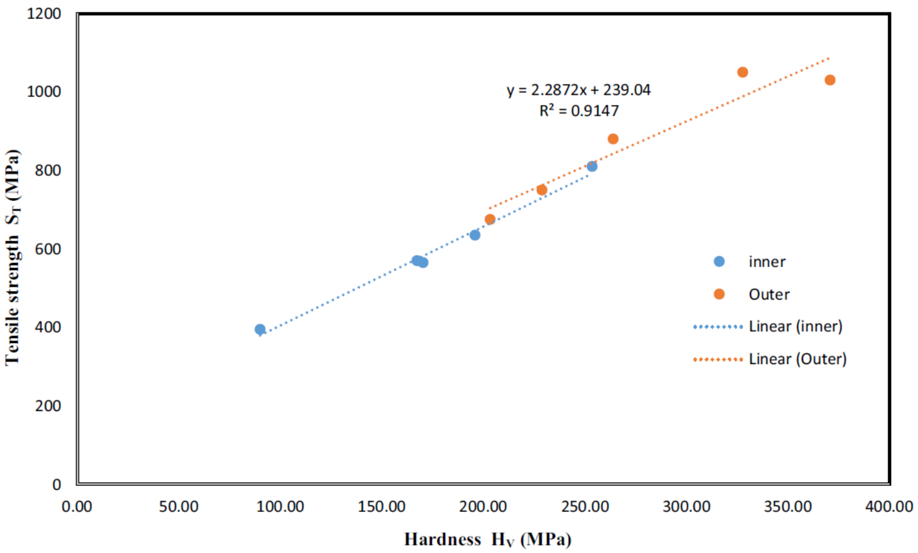


Fig. 3 Graph presenting the correlation of hardness and strength of *Achatina Fulica* shell



the coefficients of correlation for both the inner and outer structures were relatively high. The applied force had a significant effect on shell microhardness; the microhardness increased with a corresponding increase in indentation test load for both inner and outer structures, which is in accordance with the power law.

The shell is an outer skeleton or exoskeleton, which is crucial for protection against the elements and provides protection for snails [2, 22]. The microhardness values are evidence of high hardness property, which enables resistance to the aforementioned external forces. The lower hardness properties of the inner structure (nacreous) provide better comfort for the flesh of the animal. The hardness property of the shell makes it a suitable material that may be used as a nano-filler to reinforce polymer materials for the development of composites or biocomposites.

3.3 Correlation Between Hardness and Strength

Figure 3 presents the hardness and strength correlation of the outer and inner structure of the shell. A significant linear correlation coefficient was observed and the prismatic layer exhibited higher strength than the nacreous layer.

This trend corresponding to the hardness regression is illustrated in Fig. 2. Furthermore, this suggested that the prismatic layer had better resistance to plastic deformation than the nacreous layer. A noteworthy increase in strength with a corresponding increase in hardness values was observed. This is evidence that the hardness properties of both layers correlated well with tensile strength. Hardness has been directly linked to numerous properties which include resistance to plastic deformation, resistance to scratch, indentation, and abrasion [10]. The resistance to indentation and plastic deformation confirmed the link between hardness and tensile strength. Furthermore, the better quality of mechanical properties identified in this shell makes it suitable for use as micro- or nano-filler reinforcement for polymer composites. The dispersion of the shell particles in a matrix may lead to the production of composite materials with excellent mechanical properties.

4 Conclusions

This study was an evaluation of the potential for beneficiation of waste *Achantina Fulica* snail shells to reduce the accumulation of waste shells in the environment after consumption of the snails. The properties and characteristics of that were studied included the following:

- Indentation
- Microhardness
- Morphological characteristics, and
- Tensile strength.

The results showed that:

- Satisfactory hardness values with high correlation coefficients were ascertained.
- The outer prismatic layer of the shell exhibited higher resistance to indentations loading than the inner layer.
- Resistance to indentation decreased with a corresponding increase in loading.
- A linear correlation of hardness and tensile strength was observed
- The prismatic layer exhibited higher strength compared to the nacreous layer of the shell.
- SEM images of the nacreous layer exhibited an aragonite platelet layer structure that presumably serves as reinforcement that supports the prismatic layer, which reduced plastic deformation of the shell resulting in relatively high resistance to indentation and plastic deformation.

These results suggest that the snail shells could be used as a filler material (micro- or nano-size) for reinforcement of polymer materials in the development of composites or biocomposites. The structural formation of *Achatina Fulica* shell could be a mimic for design synthetic processes to fabricate new bioinspired composites or nanocomposites with enhanced properties.

5 Future Research

The completion of this research brought forth certain boundaries and consequently provides opportunities for more research work. The size of the *Achatina Fulica* shell is the main drawback. Therefore, the optimization of processes for synthesizing micro- or nanoparticle from *Achatina Fulica* shell is a potential area to be explored. The imitating of *Achatina Fulica* shell morphology for design synthetic processes to fabricate new bioinspired composites or nanocomposite with required properties may also be another area for future research.

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CHAPTER FOUR: CHEMICAL CHARACTERIZATION OF *ACHATINA FULICA* SHELL FOR BENEFICIATION INTO BIOCOMPOSITE MATERIALS.

4.1 OVERVIEW

This chapter investigates the Achatina Fulica shell's chemical characterization to identify the functional group, elemental composition, carbonate ion, and mineral present in the shell. The chemical characterization was analyzed using Fourier transform infrared (FTIR), scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDX), and X-ray diffraction (XRD). Thermal properties such as thermal stability and degradation of *Achatina Fulica* shells were investigated to determine mass loss and heat flow rate. Fourier transform infrared (FTIR) spectral analysis indicated that the shell contains calcium carbonate ($CaCO_3$), with a high concentration of carbonate ions (CO_3^{2-}). X-ray diffraction (XRD) revealed that the polymorph form of calcite dominated the chemistry of the shell. Energy Dispersive X-ray Spectroscopy showed a high carbon, oxygen, and calcium level, which are the main elemental composition of the shell. The results showed that the *Achatina Fulica* shell possesses excellent thermal stability and lesser mass loss. The result of these characterization shows that the *Achatina Fulica* shell may be used to produce low-cost biofiller and calcium carbonate (CaCO3) that can serve as an alternative to the commercial fillers that are expensive. The high presence of calcium carbonate in the shell also justifies thermal stability and lesser mass loss.

Keywords:
Achatina Fulica shell, calcium carbonate ($CaCO_3$), elemental composition, carbonate ion, and minerals.

4.2 INTRODUCTION

Calcium carbonate ($CaCO_3$) filler composite is widely acceptable for different applications in the marine, automobile, mass transit, and aerospace industries [153, 195]. This suitability could be related to the improved thermal, physical, mechanical properties offered by the composite materials. The loading of $CaCO_3$ plays a significant role, such as composite bonding systems improvement, which eventually provides a more reliable and durable structure, favorable for enhancing thermal, impact resistance, and mechanical properties [153, 196, 197]. The reinforcement effectiveness of commercial $CaCO_3$ such as talc, montmorillonite, and kaolinite extent its application to the papermaking industry. The researcher confirmed that filler is often incorporated to reduce expensive matrices and improve properties [42, 198]. These carbon-based fillers are synthesized from various nanotechnology methods and evaluate the particle sizes, chemical and thermal properties [199-201]. It is either sourced from rock or natural materials, including but not limited such as animal shells and bone.

The commercial $CaCO_3$ is synthesized from the rock using either gas pressure blasting or explosion method [155, 156, 164]. Although they are mainly in the form of milled $CaCO_3$ (GCC) or precipitated $CaCO_3$ (PCC), however, PCC is usually used in composite development due to its smaller particle, which eventually helps in improving mechanical properties [202, 203]. Despite the reinforcement effect of the precipitated $CaCO_{3,}$ it contained some toxic element that is harmful to human health and not suitable for biocomposite [204-207]. This drawback attracted innovative means of producing $CaCO_3$ from agricultural waste, especially from snail shells using different techniques [200, 208]. Several studies have investigated the chemical, physical, and reinforcement of calcium carbonate of different particle sizes produced synthesized for the natural sourced and compared with commercial $CaCO_3$ [185, 209-211].

Kolawole et al.[185] synthesized $CaCO_3$ from Archachatina marginata bio-shells investigated the chemical, thermal, and physical properties of the shell and used it as reinforcement in metal matrix composite. The results gathered proved that the snail shell possesses chemical hard phase oxides with good suitable reinforcement potential, higher thermal stability, and material degradation, indicating filler material to serve as an alternative to commercial $CaCO_{3.}$

Similarly, Asafa et al. [209] examine the reinforcement potentials of Snail shell on discarded aluminum-based composite materials where aluminum serves as the matrix, and snail shell particle serves a biofilter. Shell particle sizes of 200, 400, and 600 µm were incorporated at different loading ratios ranges from 16-48%. The composite material was investigated for tensile strength and hardness properties. According to the result, the reported loading of snail shell particles improved both properties significantly. Research proved that more than 200,000 species of snail shells are available in the world [212]. In most of the available reports on snail shell properties or composite, authors do not identify the specific shell used for their investigation. Although there are pieces of literature on the fundamental properties of the shell, most of the snail shell species are not yet investigated

Hence, this present study investigated the thermo-chemical characterization of the *Achatina Fulica* shell to determine the carbonate mineral, the content of $CaCO_{3,}$ as these are the fundamentals that determine reinforcement suitability for the development of biocomposite.

4.3 MATERIALS AND METHODS

The shell (*Achatina Fulica*) collected from the University Kwazu-natal, Westville campus soccer pitch was used for this study. It was kept under room temperature for 24hours to dry before milling. The dry shell (30g) was placed in a 500ml stainless jar (inner diameter of 100mm), together with stainless steel balls (10mm diameter). Subsequently, the shell was dry-milled in a planetary ball mill (Retsch ® PM 100). The grinding operation involved milling at 400 rpm for 30 minutes in a clockwise direction. The collected shell powder was sieved using a mechanical sieving shaker (Retsch, AS 200 basic, Germany) to a particle size of ≤ 25 μm, and fine particle size was used for XRD and FTIR investigation.

Infrared spectra were measured to identify the shell (*Achatina Fulica*) functional group using a Perkin Elmer Universal ATR spectrometer. X-ray diffraction (XRD) was conducted to determine carbonate minerals present in the shell. A diffractometer (PANalytical Empyrean instrument; Co radiation 1.54056Ä) recorded XRD patterns and analyzed between 0-90^0 (2ϴ) at voltage, current, and past times 40 kV, 40mA, and 1 second respectively. The chemical composition of the shell was carried out using a Zeiss Evo Ls 15 scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDX).

Thermal stability and degradation of *Achatina Fulica* shell are determined using thermogravimetric analysis (TGA). The thermal Analyser (Thermal Universal V 4.5 A) instrument was used to measure thermal stability and degradation. The investigation was conducted under a dry nitrogen gas flow rate of 100 mL/min from 0^0C to 1400^0C, at a heating rate of 10 ^{0}C/min.

4.4 RESULT AND DISCUSSION

After successfully milling the *Achatina Fulica* shell into powder form, the FTIR spectra of the shell powder in Figure 4.1 shows several bends from 4500 cm^{-1} to 500 cm^{-1}.

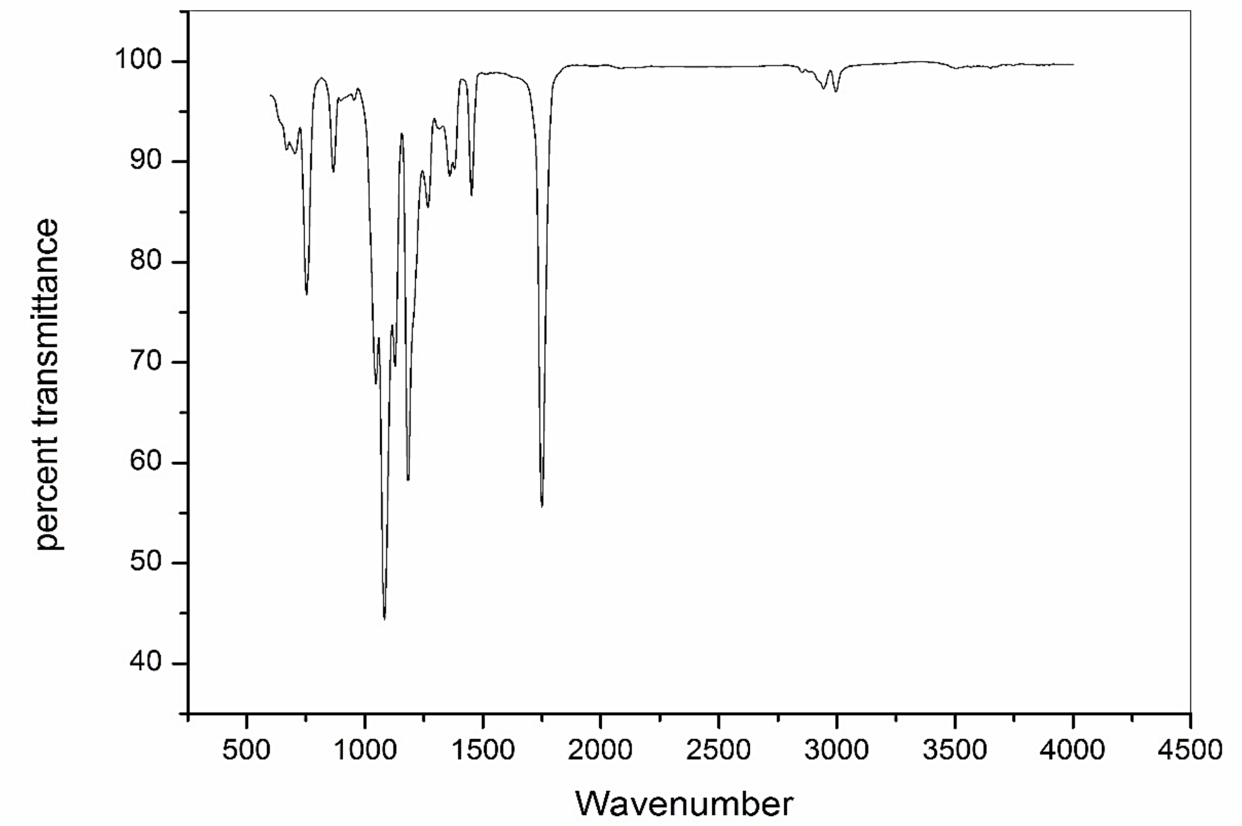


Figure 4.1: Fourier transform infrared (FTIR) spectra of the shell powder (Achatina fulica).

The characteristic absorption bands for carbonate ions ($CO_3{}^{2-}$) were observed at 713, 874, 1010, 1097,1105, 1220, 1496, 1789 cm^{-1} respectively. The spectra showed that the absorption peak of 713 cm^{-1} might be attributed to the 4the in-plane bending of the carbonate ion, while the absorption peak observed at 874 cm-1 may be recognized due to the out-of-plane bending vibration carbonate ion. The broadband at 1097 cm^{-1} indicated a carbonate ion ($CO_3{}^{2-}$) and was found to be intense in the shell. calcite [168, 213-215].

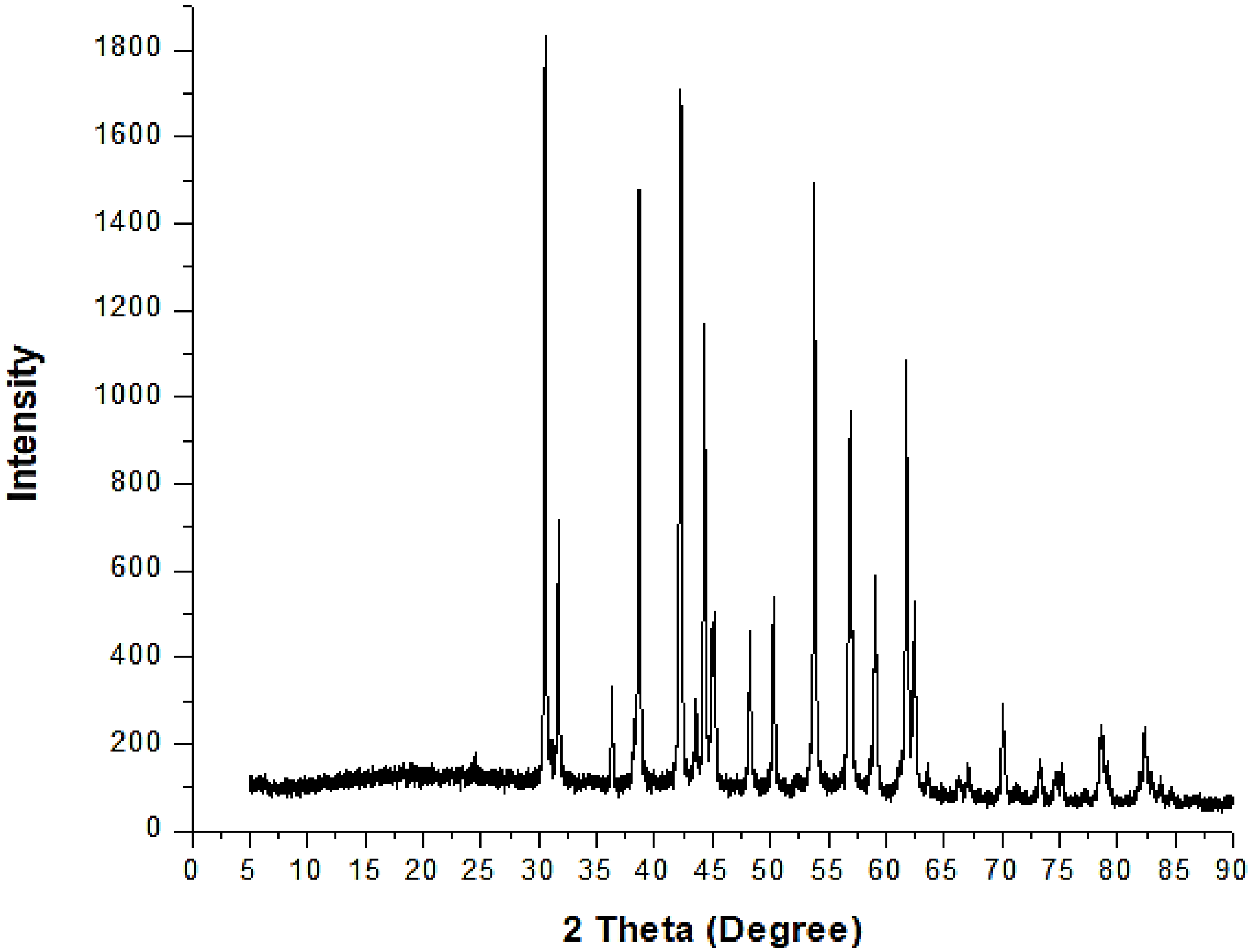
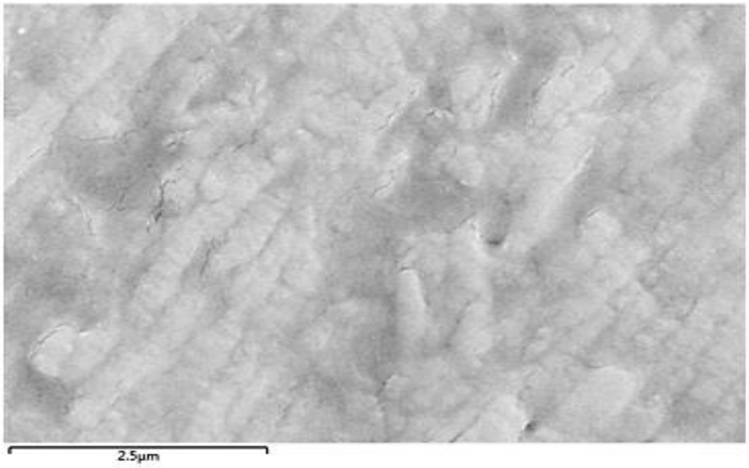
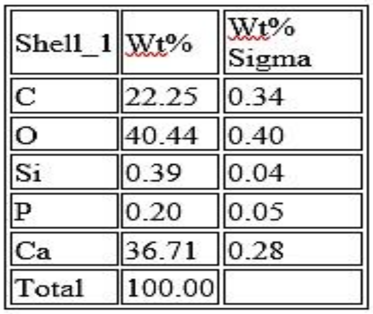


Figure 4.2: X-ray diffraction (XRD) of the shell powder (Achatina Fulica).

The X-ray paradigm of Achatina Fulica shell show characteristic diffraction peaks corresponding to different diffraction angles at 31^0, 36.5^0, 39.3^0, 42.5^0, 44.5^0, 47.5^0, 47.6^0, 50.5^0, 53.4^0, 56.5^0, 62.3^0, 70^0, 73^0, 75.2^0, 78.3^0, and 82.5^0. These characteristic diffraction peaks show that calcium carbonate exists as polymorphism such as calcite, aragonite, and vaterite in this shell; however, the polymorph form of calcite dominates. It is well known that carbonate mineral is hard and has better heat resistance. The characteristic of this shell may be favorable for improving the mechanical and thermal properties of polymeric material.





Shell_1	Wt%	Wt% Sigma
C	22.25	0.34
O	40.44	0.40
Si	0.39	0.04
P	0.20	0.05
Ca	36.71	0.28
Total	100.00	

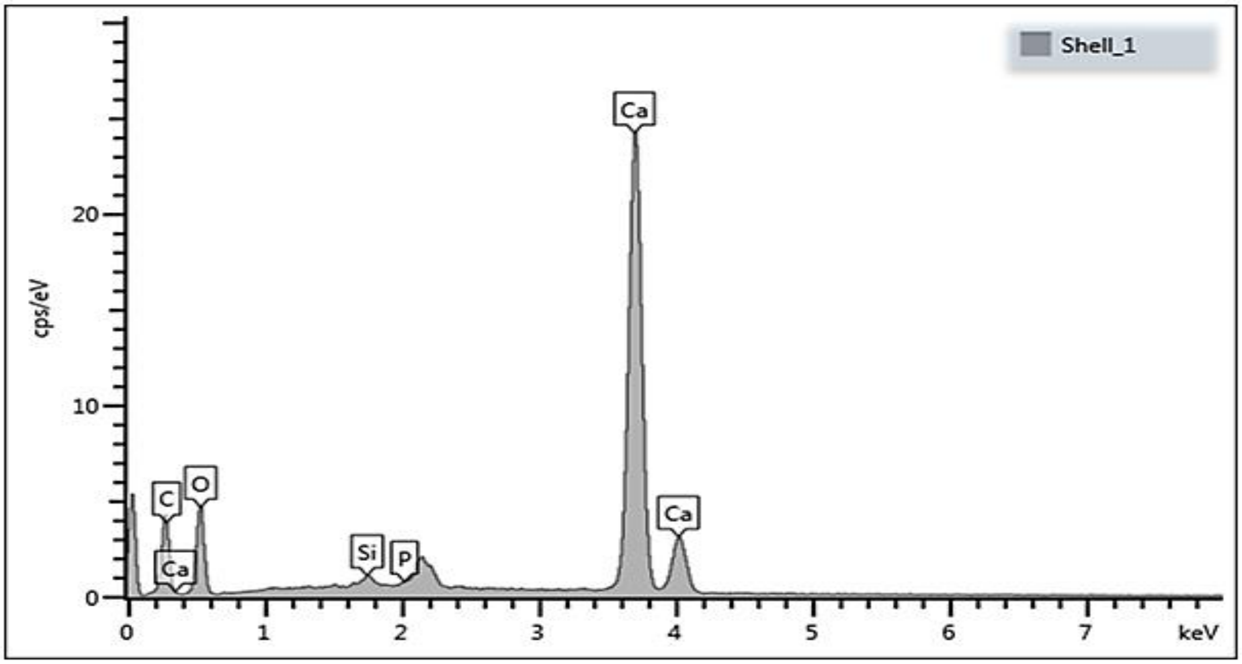


Figure 8: EDX Spectroscopy of Achatina Fulica shell

The Energy Dispersive X-ray Spectroscopy in figure 4.3 shows the elemental composition of the shell. High levels of carbon, oxygen, and calcium are evident, which is attributed to the main component of

Achatina Fulica shells, being calcium carbonate. This corresponds with the trend observed in Figures 4.1 and 4.2, which proves that Achatina Fulica shell can produce $CaCO_3$ at a bit of cost, which may eventually reduce the cost of production of new material with improved properties.

4.4.1 Thermal properties

The thermal stability and degradation of the *Achatina Fulica* shell studied using thermogravimetric analysis (TGA) was shown in Figure 4.3. The curves show two thermal events within the temperature range of 0-1400^{0}C. The first phase (608.37^{0}C) is exothermic. This thermal performance is ascribed to the decomposition of organic substances, which eventually causes a slight weight loss (1.22%). The second phase (803.01^{0}C) is endothermic and is linked to the decomposition of calcium carbonate into carbon dioxide and calcium oxide. The weight loss, in this case, was equated to approximately 41.91% of the total loss.

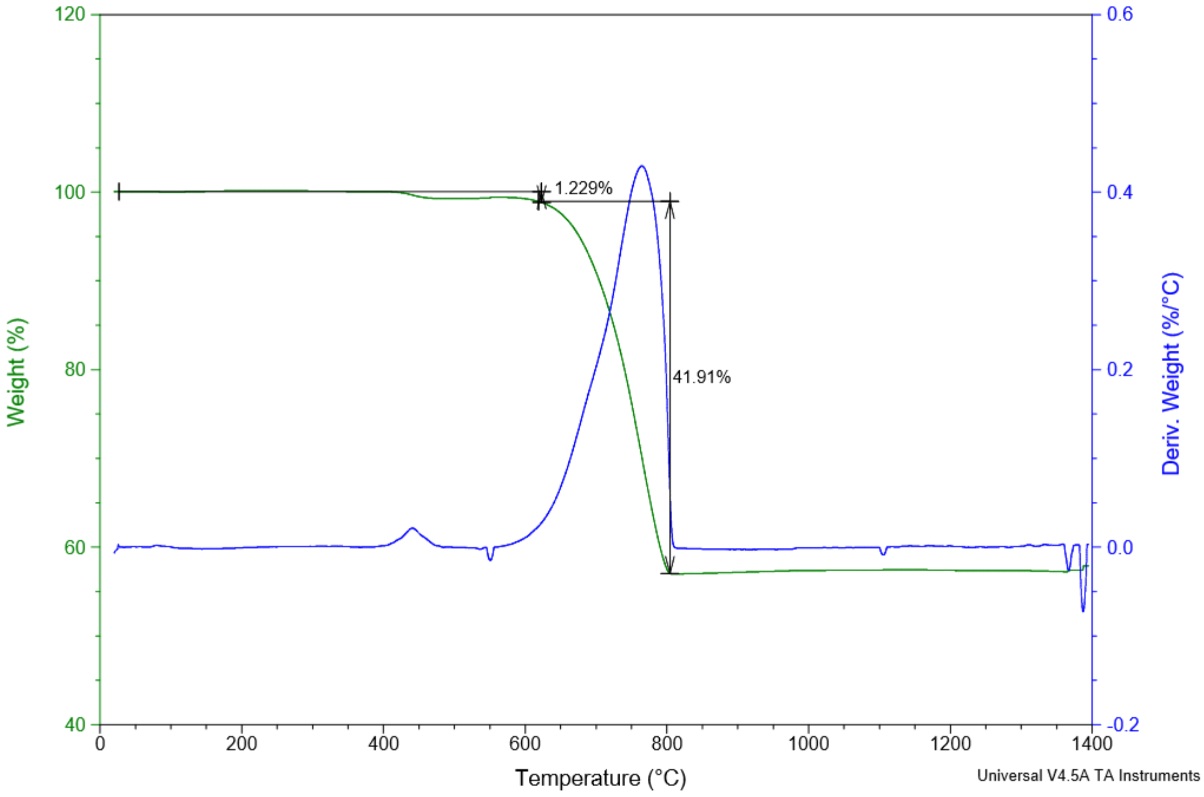


Figure 9: TGA/DSC thermogram curve of Achatina Fulica shell

The shell exhibited a low percentage of water and oil intakes, which were 0.0814 % and 0.013%, respectively. Significantly, show that the *Achatina Fulica* shell is hydrophobic. This characteristic is favorable for a potential filler in reinforcing polymer material and proves this shell's suitability as a reinforcement additive. Scanning electron microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) was conducted to determine the structural formation and elemental composition of the *Achatina Fulica* shell, which can eventually justify the sorption characteristics of the shell. Figure 4.2 shows a micrograph of the *Achatina Fulica* shell at 15.90 KX magnification. A close-pack structure formation that barely allows permeability of the solvent was observed. Although line cracks were observed, the layers formed in the shell stand as a bearer for fluid inflow, which eventually reduced sorption.

4.5 SUMMARY

This research study dealt with the Anchetina Fulica shell's chemical characterization to determine its suitability as a filler based on the following conclusions.

1. The result of this study confirmed a high concentration of $CaCO_3$ in the shell.
2. Energy Dispersive X-ray Spectroscopy showed high carbon, oxygen, and calcium levels directly attributed to calcium carbonate.
3. X-ray diffraction affirmed the existence of calcium carbonate as polymorphism such as calcite, aragonite, and vaterite in this shell, where vaterite dominated.
4. The thermograph shows that the shell exhibited excellent thermal stability and a substantial low in temperature degradation. All these elemental compositions, carbonate minerals, and ions prove that the *Anchetina Fulica shell* contains a more significant amount of calcium carbonate.

All these suggested that *Achatina Fulica* shells have required thermal and calcium carbonate content suitable for producing and producing biofiller for biocomposite applications. The following section provides information on synthesizing different particle sizes of $CaCO_3$ from *Achatina Fulica* shells and their reinforcement potentials.

CHAPTER FIVE: OPTIMIZATION OF MILLING PROCEDURES FOR SYNTHESIZING NANO- $CACO_3$ FROM *ACHATINA FULICA* SHELL THROUGH MECHANOCHEMICAL TECHNIQUES

Author contribution:

Gbadeyan O.J *conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript*

Onwubu S. *allowed us to use his laboratory and ball milling equipment for producing nano-*$CaCO_3$ *from Achatina Fulica shell*

Prof. S. Adali, Prof. G. Bright, and Prof. B. Sithole *provided material and equipment used for experimenting, supervised all process, and proofread the manuscript*

5.1 OVERVIEW

The information on the possibility of obtaining calcium carbonate nanoparticles from the *Achatina Fulica* shell is provided in this chapter. It also details the stages of obtaining calcium carbonate nanopowders from shell collection, treatment, and milling processes. The process of characterizing Achatina Fulica shell particle size and shape using Transmission electron microscopy and an iTEM image analyzer is provided. The effect of solvent on the chemical characteristics such as functional group, elemental composition, and carbonate ion of calcium carbonate nanopowders obtained from the *Achatina Fulica* shell is investigated. Similarly, the procedure for chemical characterization using Fourier transform infrared (FTIR) and scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDX) is given. Subsequently, the effect of the milling procedure on the mechanical properties such as tensile strength, stiffness, and hardness of prepared nanocomposites was also given. It also presents and discussed the results of the investigations conducted on the *Achatina Fulica* shell particles-filled nanocomposite.

KEYWORDS: Achatina Fulica Shell, Mechanochemical techniques, Nano-$CaCO_3$, Particle size, Mechanical properties.

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Research Article

Optimization of Milling Procedures for Synthesizing Nano-$CaCO_3$ from *Achatina fulica* Shell through Mechanochemical Techniques

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The possibility of obtaining calcium carbonate nanoparticles from *Achatina fulica* shell through mechanochemical synthesis to be used as a modifying filler for polymer materials has been studied. The process of obtaining calcium carbonate nanopowders includes two stages: dry and wet milling processes. At the first stage, the collected shell was dry milled and undergone mechanical sieving to $\leq 50\,\mu$m. The shell particles were wet milled afterward with four different solvents (water, methanol, ethylene glycol, and ethanol) and washed using the decantation method. The particle size and shape were investigated on transmission electron microscopy, and twenty-three particle counts were examined using an iTEM image analyzer. Significantly, nanoparticle sizes ranging from 11.56 to 180.06 nm of calcium carbonate was achieved after the dry and wet milling processes. The size particles collected vary with the different solvents used, and calcium carbonate synthesis with ethanol offered the smallest organic particle size with the average size ranging within 13.48-42.90 nm. The effect of the solvent on the chemical characteristics such as the functional group, elemental composition, and carbonate ion of calcium carbonate nanopowders obtained from *Achatina fulica* shell was investigated. The chemical characterization was analyzed using Fourier transform infrared (FTIR) and a scanning electron microscope (SEM) equipped with an energy-dispersive spectroscope (EDX). The effect of milling procedures on the mechanical properties such as tensile strength, stiffness, and hardness of prepared nanocomposites was also determined. This technique has shown that calcium carbonate nanoparticles can be produced at low cost, with low agglomeration, uniformity of crystal morphology, and structure from *Achatina fulica* shell. It also proved that the solvents used for milling have no adverse effect on the chemical properties of the nano-$CaCO_3$ produced. The loading of calcium carbonate nanoparticles, wet milled with different solvents, exhibited different mechanical properties, and nanocomposites filled with methanol-milled nano-$CaCO_3$ offered superior mechanical properties.

1. Introduction

Nanosized calcium carbonate ($CaCO_3$) has received noteworthy consideration for several applications due to its availability, advantageous mechanical strength, and thermal stability [1]. It is commonly used as filler or reinforcement for polymeric materials, papers, and paints. This carbon-based material is obtained from several resources such as rock, humans, and animal waste through different methods. Over many decades, montmorillonite and kaolinite with a high concentration of $CaCO_3$ commonly referred to as nanoclay are commonly used and soured from rock and synthesized using either gas pressure blasting or explosion method [2–4]. Studies conducted confirmed the effectiveness of nanoclay in improving several composite properties [5, 6]. However, it has been discovered that the end-of-life of the composite produced with nanoclays tends to have negative impacts on human health, and, at times, the composite is more expensive when compared to naturally sourced fillers [7]. These drawbacks consequently have reduced the use of this filler in some countries.

The harmful impact of the abovementioned fillers and factors such as climate change compelled materials scientist to source for alternative filler material. The fillers are sourced from natural resources that not only offer suitable filler material properties but also meet societal needs and support global sustainability. Consequently, in recent decades, calcium carbonate ($CaCO_3$) of different particle sizes extracted from natural resources such as bones, horns, and animal shells is used as reinforcement to enhance thermal stability, degradation, strength, and physical properties of polymeric materials [8].

Several types of research have investigated the functional group, elemental composition, and minerals present in eggshell, mollusk shell, and animal bone [8–11]. These natural resources were discovered to have a higher content of calcium carbonate ($CaCO_3$), especially eggshell, which was confirmed to have about 95% of $CaCO_3$ [12–14]. Furthermore, mollusk shell, oyster shell, and animal bone have been investigated for $CaCO_3$, and they were found to have adequate filler-appropriate properties for different applications. Consequently, calcium carbonate produced from animal waste has been suggested to be used as an alternative to commercial $CaCO_3$ for some applications, which include but not limited to the dental and medical applications [8, 9, 15–18]. The mechanism behind the physical properties of shell structure has been studied [19, 20]. Filetin et al. [19] investigated microhardness of *Pinna pectinata* (Pinnidae), with the Adriatic Sea mollusk shell structure as a function of the indentation load. The result proved that the microhardness of the shell depends on the load for the nacreous (inner layer of the shell) and prismatic (outer layer of the shell) structures. Furthermore, the microhardness value measure for the outer layer was higher than that for the inner layer with a lesser margin. Besides, a notable aragonite platelet structure was seen in between the nacreous and prismatic predominant normal stress, preventing interlamellar sliding/plastic deformation of the shell. This study was consistent with our previous investigation on the physical and morphological study of *Achatina fulica* shell. The layer of aragonite was referred to as reinforcement and served as the main functional mechanism that prevents plastic deformation which resulted in high resistance to indentation, resulting in relatively high microhardness and tensile strength properties [20]. However, there is limited literature about $CaCO_3$, synthesized from these natural resources, being used either as a filler material to fabricate composite or as polymer material reinforcement. This output may be because milling a large quantity of these materials to smaller particle sizes comes with many challenges, which include but not limited to particle agglomeration.

Despite the availability of numerous milling techniques used for small organic particle synthesis, the mechanochemical technique has been found to be most effective [4, 21]. This organic synthesis mechanism has been regarded as a significant change towards achieving the sustainable and efficient process of producing small molecular sizes of grains [22]. Numerous researchers confirmed that mechanochemical techniques are a branch of chemistry that covers any chemical transformations induced mechanically or physiochemical changes of the material of any state of combination due to the influence of mechanical energy such as friction, compression, or shear [15, 23–26]. A mechanochemical procedure such as hand grinding or ball milling has been reported to influence the structure and composition of materials. Consequently, it brings about an opportunity for the preparation and fabrication of nanomaterial particles using top-down tactics [27].

Ball mill is a high-energy mill process especially used for an energy-intensive process like mechanical alloying, mechanochemistry, or mechanical activation. Planetary ball mill is used to determine the dependence of process efficiency using milling parameters such as ball size and number, mill geometry, and velocity of the rotating parts. However, the maximum efficiency of the grinding process achieved with high-density balls, and higher rotation speed seems to provide materials with higher impact energy in comparison with small, low-density balls and lower rotation speed [28, 29].

The planetary ball mill theory and its efficient procedure for producing small molecular sizes of grains achieved using the mechanochemical technique made it a promising candidate for solvent-free synthesis [21, 30, 31]. However, solvent-free synthesis may not apply to all materials, especially calcium carbonate-based materials, where the agglomeration of particles is dominant. Research studies have proved that dry milling technique causes a large agglomeration of the particles during synthesis. Most times, this results in a bimodal size distribution, which weakens the bond in nanocomposites [32–35]. Having this in mind, this present study deals with the optimization of milling procedures for synthesizing nano-$CaCO_3$ from *Achatina fulica* shell through mechanochemical (wet milling) techniques using different solvents. It further investigates the consequence of the solvent on the reinforcement effect of the nano-$CaCO_3$ on polymeric material.

2. Experimental Details

2.1. Raw Material Collection, Preparation, and Synthesis. Epoxy resin and hardener supplied with the trade name of LR 30 and LH 30 (medium) was used as a binder.

Achatina fulica snail shells collected from the University of Kwazulu-Natal, Westville campus soccer pitch, were washed and disinfected. Snail shells were soaked in a solution of water and 5% diluted household sodium hypochlorite for seven hours. Afterward, they were rinsed with distilled water and dried in the oven at 150°C for 20 mins to ensure absolute dehydration.

2.1.1. Nano-$CaCO_3$ Synthesis. The clean shells were kept under room temperature for 24 hours to dry before milling. The milling process was done in two stages. The first stage was dry milling, and the second was wet milling. At the first stage, 30 g of dried *Achatina fulica* snail shells was measured and dry milled in a planetary ball mill (Retsch® PM 100) to obtain fine particles [12, 36]. The milling setup comprises

50 stainless steel balls of 10 mm diameter and a 500 mL stainless steel jar (inner diameter of 100 mm). The snail shells were milled at 450 rpm for 30 minutes in a clockwise direction. The shell powder after the milling process was sieved using a mechanical sieving shaker (Retsch, AS 200 basics, Germany) to a particle size of ≤50 μm. In the second stage, the collected snail shell powder was wet milled to achieve nanoparticles. Accordingly, 30 g of snail shell particle size of ≤50 μm was measured into the 500 mL stainless steel jar. After that, 100 mL of a different solvent such as water, methanol, ethylene glycol, and ethanol was added differently and wet milled at 450 rpm for 258 mins in a clockwise direction. Subsequently, mixtures of fine particles and solvent were separated by removing the liquid layer that is free of a precipitate using the decantation method. To ensure the total removal of the solvent, settled particles were washed by adding distilled water and separated using the decantation method. This process was repeated five times to ensure the cleanness of fine particles. Then, particles were dried in the oven at 35°C for 72 hours. The fine powders obtained after that were characterized to establish the successful synthesis of the $CaCO_3$.

2.2. Characterization Approaches

2.2.1. High-Resolution Electron Microscopy. The particle size, shape, and distribution of snail shell particles milled with different solvents were observed under a transmission electron microscope (TEM). The investigation was conducted on JEM Jeol 2100 (Japan). Before this investigation, a small amount of snail shell powder was dispersed in 10 mL of ethanol and sonicated at 10 kV for 10 mins. Afterward, a thin cross section of cryomicrotomed specimens was prepared using a Leica microtome and placed on carbon copper grids. The TEM image was further analyzed on iTEM analyzer software, version 5.0.1 (Japan), to determine the range of particle sizes.

2.2.2. Fourier Transform Infrared Spectroscopy. The Fourier transform infrared (FTIR) spectra were measured to identify the functional group constituents of snail shell particles milled with different solvents. A PerkinElmer Universal ATR spectrometer was used for investigation. A small quantity of each sample was placed in the sample pouch. Subsequently, an initial background check was conducted before scanning within the range of 550-4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.2.3. Scanning Electron Microscope. The chemical composition of the shell was determined on the Zeiss Ultra FEG-SEM field emission scanning electron microscope (SEM) equipped with an energy-dispersive spectroscope (EDX). Before SEM (field emission, Carl Zeiss) observation, the surface was coated with a thin, electric conductive gold film to prevent a buildup of electrostatic charge.

2.2.4. Nanocomposite Preparation. Nanocomposites were prepared using the conventional resin casting method. To facilitate shell particle dispersion and to reduce matrix viscosity, 100 wt.% of epoxy resin was measured into the beaker using a Snowrex digital electronic scale with 0.1 g and heated up to 70°C. Subsequently, 2 wt.% of $CaCO_3$ nanoparticles from shell particles was slowly incorporated into the matrix and mixed using a mechanical stirrer at 500 rpm for one hour to ensure homogeneous dispersion of shell particles. Nanocomposites were taken off the stirrer and were allowed to cool down to room temperature. Then, the catalyst was added to nanocomposites at a mixing ratio of 100-30 wt.%. The blend was thereafter poured into an open mold to have a composite panel and allowed to cure for two days. To facilitate the easy removal of the nanocomposite panel, the wax was applied to the inner surface of the plastic mold before pouring. The mechanical strength of the fabricated nanocomposite panel was investigated after 15 days.

2.3. Mechanical Testing. Mechanical tests such as tensile, hardness, and impact were performed on wholly cured composite panel samples obtained after fifteen days of casting.

2.3.1. Tensile. The tensile strength and stiffness of nanocomposite were determined according to the ASTM D3039 test standard. The test was carried out on samples using a Lloyd universal testing machine (Model 43) fitted with a 30 kN load cell. Five samples were tested at ambient temperature, and the constant crosshead speed of testing used was 1.3 mm/min. The mean value of the five samples was reported.

2.3.2. Hardness. The Barcol impressor hardness tester commonly used for composite material was used to determine the hardness property of composite panel samples. The test was performed according to the ASTM D2583 test standard. A standard impressor with a steel truncated cone (6.82 height and a tip diameter of 0.55 mm) was used at an angle of 26°. This intender was positioned on the surface of the composite panel, and a uniform downward press was applied by hand, and readings were collected directly from the dial indicator. Twenty-five indentation readings were randomly collected on the sample, and the mean values were used for graphical illustration and discussion.

3. Result and Discussion

3.1. Characterization. Figure 1 presents the FTIR spectra of the raw snail shell (*Achatina fulica*) powder and $CaCO_3$ nanoparticle obtained through ball milling mechanochemical techniques using different solvents. Numerous bands were seen within the range of 550 cm^{-1}-4000 cm^{-1}.

A relatively few FTIR spectra peaks, typically associated with the stretching vibration of the functional group, were observed.

Noticeably, the spectra for the raw shell and synthesized nano-$CaCO_3$ are quite different within the functional group region. On the contrary, insignificant different FTIR spectra peaks and bends were observed between nano-$CaCO_3$ wet milled and synthesized with different solvents such as ethylene glycol, ethanol, water, and methanol. Furthermore, the raw shell FTIR spectra display absorption peaks of calcite at about 713 cm^{-1} and 873 cm^{-1}, while nano-$CaCO_3$ synthesized with different solvents such as ethylene glycol, ethanol, water, and methanol shows the absorption peaks of aragonite at around 712 cm^{-1}, 854 cm^{-1}, and 1083 cm^{-1}. The peaks of

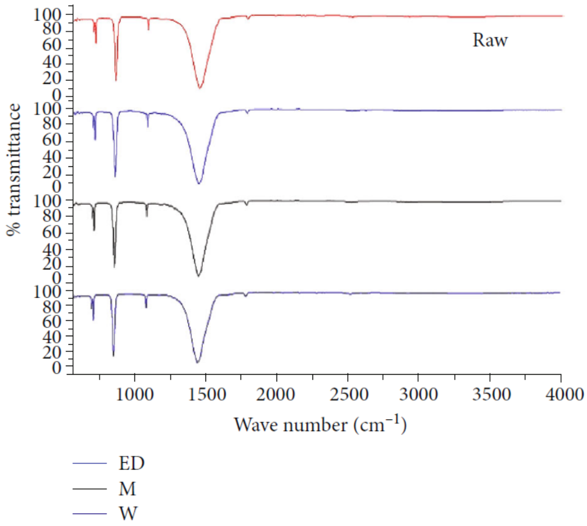


Figure 1: Fourier transform infrared (FTIR) spectra of the raw snail shell and snail shell milled with ethanol (E), ethylene glycol (ED), methanol (M), and water (W).

calcite displayed at 713 cm^{-1} and 873 cm^{-1} were accredited to the out-of-plane bending and in-of-plane bending vibration modes, asymmetric and symmetric stretching for calcium carbonate (CO_3^{2-}) molecules.

Furthermore, a very close prominent absorption peak is observed for both the raw shell powder and the synthesized $CaCO_3$ nanoparticle (1474 cm^{-1} and 1448 cm^{-1}) at the functional group region. These were associated with the presence of carbonate ions in both materials. The FTIR spectra observed for the raw shell powder were consistent with the literature for calcite [12, 16, 37, 38]. The absorption peaks of aragonite displayed at around 1083 cm^{-1} of $CaCO_3$ nanoparticles synthesized with different solvents such as ethylene glycol, ethanol, water, and methanol could be attributed to symmetric carbonate stretching vibration, and the absorption peaks of aragonite displayed at around 854 cm^{-1} were accredited to carbonate out-of-plane bending vibrations [37–39]. Additionally, the carbonyl group C=O bending identified around 1788 cm^{-1} was attributed to solvent (ethylene glycol, ethanol, water, and methanol) used for mechanochemical processes. Similarly, the tiny slope of carboxyl group O-H stretching is observed at around 2533 cm^{-1}. This is associated with traces of water molecules. This suggests that $CaCO_3$ nanoparticles can be obtained from snail shell *Achatina fulica* using wet milling with ethylene glycol, ethanol, water, or methanol using mechanochemical procedures.

The elemental composition of the raw snail shell and $CaCO_3$ nanoparticle synthesized with different solvents such as ethylene glycol, ethanol, water, and methanol is shown in Table 1. An elemental composition such as carbon, oxygen, and calcium dominated different weight percentages in both raw snail shells and the synthesized nano-$CaCO_3$. It was observed that the raw snail contains a high volume of $CaCO_3$ of about 99.4 wt.% and other metal oxides of about 6 wt.%. However, this was lesser compared to the synthesized nano-$CaCO_3$ that has 100 wt.% $CaCO_3$ irrespective of the solvent used for the wet milling process. This may suggest that the mechanochemical procedure used to synthesize helps in achieving small molecular nanoparticles and the decantation method adopted also helps in purification of the nanoparticle, resulting in clean 100 wt.% $CaCO_3$.

This performance may be a result of the milling period and solvent used. Among the nano-$CaCO_3$ synthesized with different solvents and raw snail shells, water-synthesized nano-$CaCO_3$ contains the highest amount of carbon, which eventually reduces the weight percentage of oxygen and calcium present in the material. The weight percentage of these components suggests that the use of water increases the carbon content in the synthesized $CaCO_3$, which make it harder than others; this fact can be related to the mechanical property improvement observed in Figures 2–4.

Table 2 presents particle sizes of the synthesized $CaCO_3$ nanoparticles that were investigated using iTEM Jeol 2100 HR (high resolution). To determine the appropriate solvent for optimizing the wet milling method for producing nano-$CaCO_3$, TEM images were further analyzed under TEM image analyzer software version 5.0.1 on volume base. Significantly, 28 counts of $CaCO_3$ particle sizes randomly selected were investigated against each solvent used. Figure 5 shows the TEM image analysis for $CaCO_3$ powder obtained, and the means of the powder consisted of 25.35 nm–63.68 nm sizes of a particle having semisphere morphology.

The particle size of ethanol-synthesized $CaCO_3$ ranges from 13.43 nm to 42.56 nm, ethylene glycol-synthesized $CaCO_3$ ranges from 11.56 nm to 65.78 nm, methanol-synthesized $CaCO_3$ ranges from 12.57 nm to 98.66 nm, and water-synthesized $CaCO_3$ ranges from 24.29 nm to 180.06 nm. Notably, nanosized particles within the range of 100 nm were observed for all synthesized $CaCO_3$. However, water-synthesized $CaCO_3$ has the biggest particle size of 63.68 nm, considering the mean of the 25 counts, as shown in Table 2. This particle size is consistent with figure observed in Table 1, where water-synthesized $CaCO_3$ powder has high carbon content.

The presence of water mixtures has been confirmed to affect $CaCO_3$ polymorphs and morphology [40]. This fact suggests that the inclusion of water before the milling process affected polymorphs and morphology of the shell powder, which eventually prevents the effectiveness of the ball milling process, resulting in larger particle sizes. Furthermore, ethanol-synthesized nano-$CaCO_3$ has the smallest range of particle sizes. This outcome proved the effect of ethanol on breaking $CaCO_3$ molecules into small sizes. Additionally, a low standard deviation was observed for 28 counts of $CaCO_3$ particle sizes randomly selected. This consequence depicts the effectiveness of ball milling in providing uniform particle sizes that are very close to the mean value of the particle sizes.

3.2. Mechanical Properties. The reinforcement effect of synthesized nano-$CaCO_3$ using different solvents through mechanochemical was investigated. Table 3 shows that the loading of the manufactured nanoparticle enhanced the mechanical properties of the epoxy composite. This trend is consistent with previous findings.

Table 1: Elemental composition of the raw snail shell and synthesized Nano-$CaCO_3$.

Elemental composition	Raw snail shell (wt.%)	E (wt.%)	ED (wt.%)	M (wt.%)	W (wt.%)
C	36.71	29.45	27.43	18.43	50.63
O	22.25	48.98	51.52	50.41	38.42
Ca	40.44	21.58	21.05	31.16	10.95
Calcium carbonate (wt.%)	99.4 ± 0.1	100 ± 0.1	100 ± 0.1	100 ± 0.1	100 ± 0.1
Other metal oxides	0.6 ± 0.001	—	—	—	—

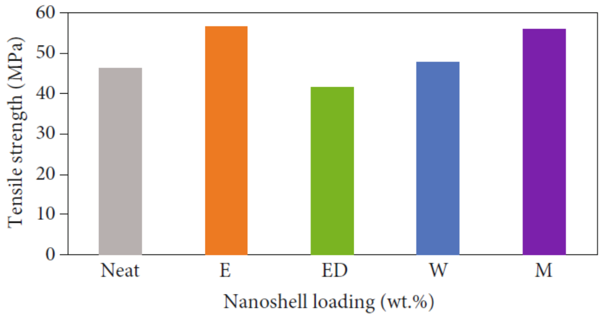


Figure 2: Tensile strength of neat and synthesized nano-$CaCO_3$-filled epoxy composites.

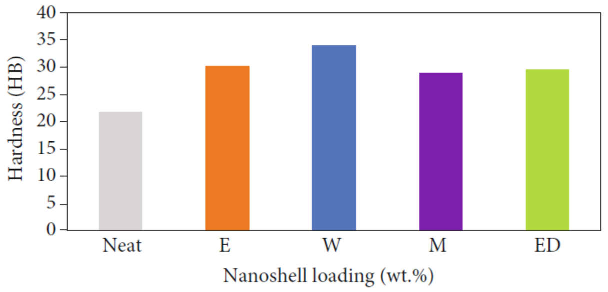


Figure 4: Hardness of neat and synthesized nano-$CaCO_3$-filled epoxy composites.

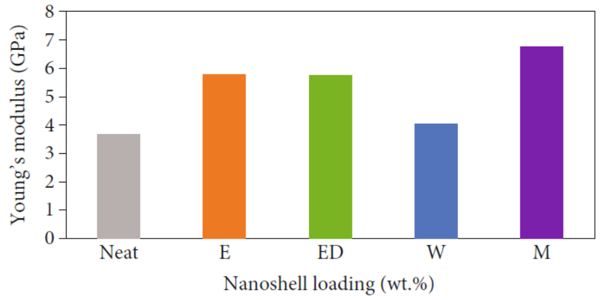


Figure 3: Tensile modulus of neat and synthesized nano-$CaCO_3$-filled epoxy composites.

Table 2: Statistical data of the particle size of $CaCO_3$ wet milled with ethylene glycol, ethanol, water, and methanol.

Base count	E (nm)	ED (nm)	M (nm)	W (nm)
Count	28	28	28	28
Minimum	13.48	11.56	12.57	24.29
Maximum	42.90	65.78	98.66	180.06
Standard deviation	8.17	14.17	27.17	35.74
Variance	66.82	200.80	738.35	1277.52
Median	25.65	31.53	46.07	54.97
Mean	25.39	32.63	51.97	63.68

This performance may be attributed to the good dispersion and interconnecting networked structure of the particles incorporated in the matrix that formed a tougher, strengthened, and stronger structure than neat epoxy. This trend is consistent with pieces of literature where filler loading enhances mechanical properties [3, 8, 41]. The mechanical property results shown in Table 3 are higher compared with those reported in some available literature where $CaCO_3$ synthesized from other shells are used to improved mechanical properties [42–44]. The loading of $CaCO_3$ synthesized from a shell such as eggshell and mollusk and milled to microparticles improved the mechanical properties; however, loading of *Achatina fulica* shell offered superior properties [45–47]. This performance may be attributed to excellent dispersion of particles in the polymeric material shown in Figure 6, which was facilitated by the small particle sizes of the synthesized calcium carbonate particles.

Nano-$CaCO_3$ produced with ethanol- and methanol-filled composites exhibited almost the same tensile strength and hardness properties, as shown in Figures 2 and 4. The loading of nano-$CaCO_3$ synthesized with ethanol improved the strength of epoxy by 22.42%, and incorporation of nano-$CaCO_3$ manufactured by methanol enhanced tensile strength by 21.34%. This improvement may be attributed to the particle size and shape of the synthesized nano-$CaCO_3$ incorporated.

Tensile strength values for the epoxy composite filled with nano-$CaCO_3$ synthesized with ethanol glycol and water are on the lower side compared to nano-$CaCO_3$ produced with the ethanol- and methanol-filled composites. On the contrary, hardness properties for nano-$CaCO_3$ synthesized with ethanol glycol- and water-filled composites were superior to those of nano-$CaCO_3$ produced with ethanol- and methanol-filled composites as represented in Figure 4. This confirmed that the loading of nano-$CaCO_3$ synthesized with ethanol glycol and water increases hardness, which makes it brittles. The brittleness of this material is the

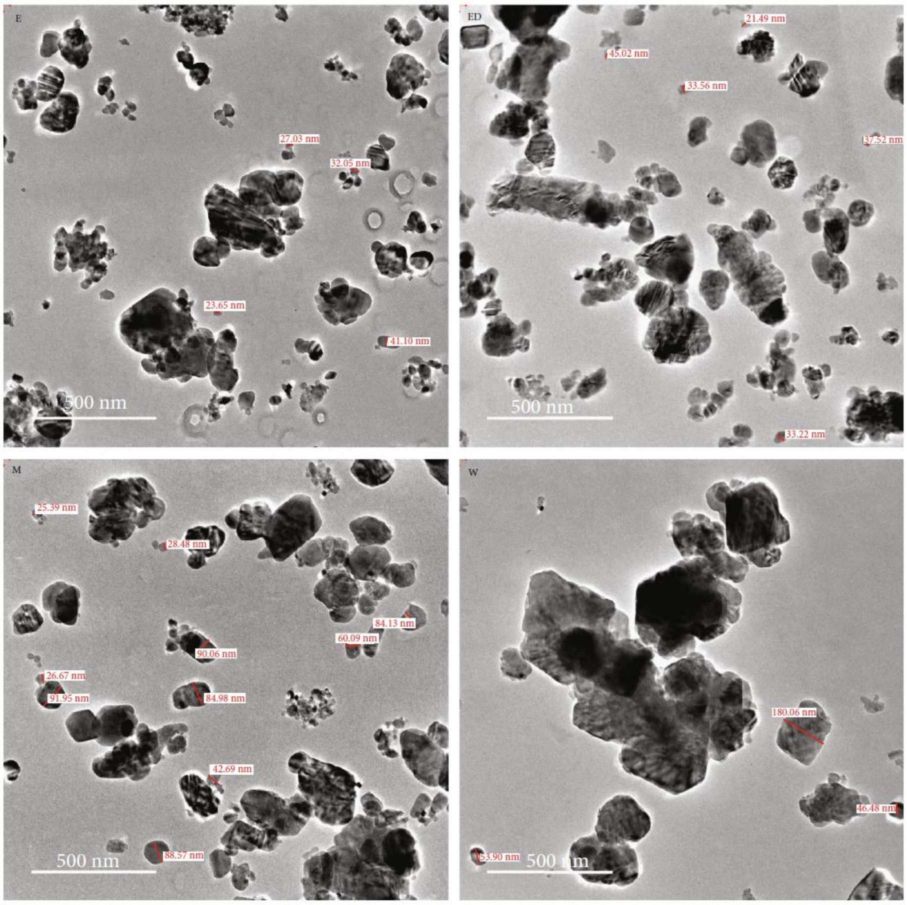


Figure 5: iTEM micrograph showing particle sizes of $CaCO_3$ obtained from ethanol (E), ethylene glycol (ED), methanol (M), water (W), and snail shell powder mixture.

Table 3: Mechanical properties of synthesized nano-$CaCO_3$-filled epoxy composite.

Samples	Tensile ultimate strength (GPa)	Young's modulus (GPa)	Hardness
Neat	46.19	3.66	21.75
E	56.55	5.77	30.15
ED	41.65	5.74	29.55
W	47.80	4.05	33.95
M	56.05	6.77	28.86

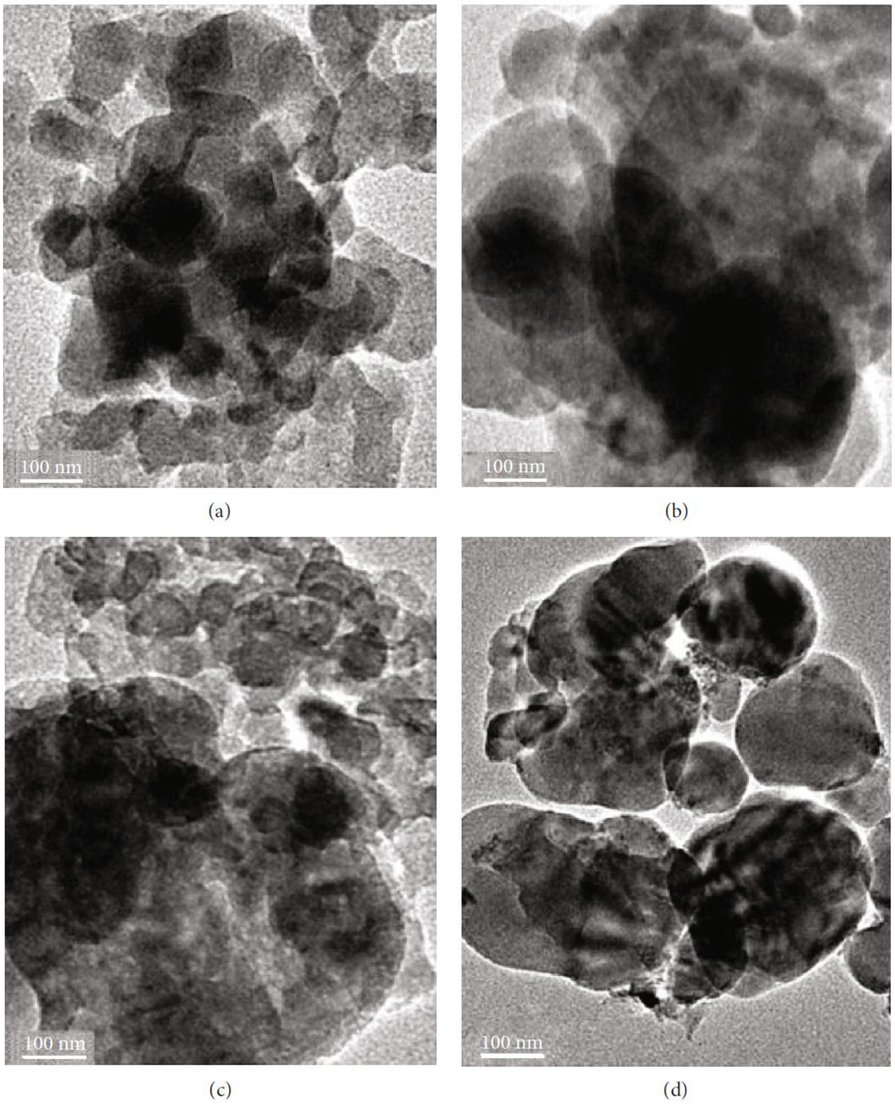
reflection of low tensile strength offered by this composite, as shown in Figure 2.

Figure 3 shows that the loading of synthesized nano-$CaCO_3$ is not only an efficient way to improve the mechanical strength of polymeric material but also enhances stiffness. The incorporation of synthesized nano-$CaCO_3$ improved the stiffness of epoxy nanocomposite irrespective of the solvent used for synthesizing the nanoparticles. The addition of nano-$CaCO_3$ synthesized with ethanol through mechanochemical techniques increased epoxy stiffness by 57.7%, and incorporation of nano-$CaCO_3$ produced with the addition of ethanol glycol enhanced the stiffness of epoxy by 56.8%. The addition of nano-$CaCO_3$ synthesized with water through mechanochemical techniques increased epoxy stiffness by 10.65%, and the loading of nano-$CaCO_3$ wet milled with methanol improved stiffness by 84.65%. Although loading of synthesized nano-$CaCO_3$ improved stiffness, the epoxy composite filled with nano-$CaCO_3$ wet milled with methanol offered superior stiffness.

TEM images presented in Figure 6 are for the epoxy polymer filled with nano-$CaCO_3$ milled using different solvents. The dark phase of the image signifies the nano-$CaCO_3$, and the lighter phase of the image signifies the polymer matrix. The TEM micrograph not only shows the well-dispersed nano-$CaCO_3$ in the matrix but also shows that the size of the nanoparticles is slightly different. This trend complements different particle sizes of synthesized nano-$CaCO_3$ shown in Table 2. Furthermore, the homogeneous dispersion of the nanoparticle shown in the TEM image formed an interlocking structure that strengthened the epoxy composite, which eventually led to the improved mechanical properties observed in Table 3.

4. Conclusion

Nano-$CaCO_3$ was successfully synthesized from *Achatina fulica* shell. The reinforcement effect of the produced



(a) (b) (c) (d)

FIGURE 6: TEM micrograph showing the dispersion of nano-$CaCO_3$ obtained from (a) ethanol- (E-), (b) ethylene glycol- (ED-), (c) methanol- (M-), and (d) water- (W-) milled snail shell powder mixture.

nanocalcium carbonate particles, wet milled with different solvents using the mechanochemical technique, was investigated. High-speed (450 rpm) balling milling machine was used to synthesize nanoparticle sizes. The mixture of 100 mL of different solvents and 30 g of raw snail powder of particle sizes ≤ 50 nm was wet milled at 450 rpm for 258 mins in a clockwise direction to produce nano-$CaCO_3$. It was discovered that nanoparticle particle sizes (25.35 nm–63.68 nm) of calcium carbonate could be synthesized from *Achatina fulica* shell using the mechanochemical wet milling technique.

FTIR spectra for the raw shell display absorption peaks of calcite at about 713 cm^{-1} and 873 cm^{-1} and were accredited to out-of-plane bending and in-of-plane bending vibration modes, asymmetric and symmetric stretching for calcium carbonate (CO_3^{2-}) molecules. On the other hand, nano-$CaCO_3$ synthesized with different solvents such as ethylene glycol, ethanol, water, and methanol shows the absorption peaks of aragonite at around 712 cm^{-1}, 854 cm^{-1}, and 1083 cm^{-1}. The observed absorption peaks were attributed to carbonate out-of-plane bending vibrations. This bending vibration proves that milling *Achatina fulica* shell to nanoparticles changed the polymorphs of the shell powder at microsize from calcite to aragonite.

The energy-dispersive spectroscope (EDX) confirmed that the mechanochemical procedure used to synthesize nano-$CaCO_3$ from *Achatina fulica* shell helped not only in achieving small molecular nanoparticles but also in purification, resulting in unsoiled 100 wt.% $CaCO_3$. TEM image analyzer results evidenced that the $CaCO_3$ powder obtained consisted of a particle size range of 25.35 nm–63.68 nm with semisphere morphology. The mechanical property results show that the loading of nano-$CaCO_3$ synthesized from *Achatina fulica* shell through the mechanochemical procedure was an effective way of modifying mechanical strength. Although loading of synthesized nano-$CaCO_3$ improved strength and stiffness polymetric material however, the epoxy composite filled with nano-$CaCO_3$ wet milled with methanol offered superior stiffness.

5. Future Work

The completion of this study brought forward some limitations that opened up opportunities for future work. The drawback included but not limited to the long milling period of the shells. Thus, the reduction of the milling process for synthesizing nano-$CaCO_3$ from *Achatina fulica* shell shall be a potential area for future work.

Data Availability

The authors have decided to deposit the data in the manuscript with the abovementioned topic in a public repository.

Conflicts of Interest

The authors declare that they have no conflict of interest as all authors are affiliated to the institution as academic staff and students.

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CHAPTER SIX: STUDIES ON THE MECHANICAL AND ABSORPTION PROPERTIES OF *ACHATINA FULICA* SNAIL AND EGGSHELL REINFORCED COMPOSITE MATERIALS

Author contribution:

Gbadeyan O.J *conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript*

Awogbemi O. *contributed by given a helping hand when developing biocomposite in his laboratory*

Prof. S. Adali, Prof. G. Bright, and Prof. B. Sithole *provided material and equipment used for experimenting, supervised all process, and proofread the manuscript*

6.**0 OVERVIEW**

Several studies confirmed the loading of eggshell particles as an effective way of improving the mechanical properties of polymeric material for biocomposite or composite applications. The authors have studied the loading of nano and microparticle sizes of the eggshell. However, no information on a comparative study on the reinforcement of *Achatina Fulica snail* (S-shell) and eggshell (E-shell). Thus, this chapter presents a comparative study on reinforcement properties of eggshell and snail shell particle size. The milling procedure of snail shells was reported in the previous chapter (5), dry and wet milling processes. This chapter uses *Achatina Fulica snail* (S-shell) and eggshell (E-shell) of ≤ 50 μm particle size of calcium carbonate synthesized from snail shells via dry milling procedure filler to fabricate composite and hybrid was deliberated. It further provides information on the process of loading *Achatina Fulica snail* (S-shell) and eggshell (E-shell) microparticle into the polymer to fabricate epoxy composites with the filler content ranging from 5 to 20% by weight. The mechanical properties such as tensile strength, Young's modulus, impact strength, hardness, and water absorption properties of the specimens evaluated experimentally were also discussed. The effect of loading *Achatina Fulica snail* (S-shell) and eggshell (E-shell) separately on mechanical properties and absorption properties of epoxy was discussed. Furthermore, this chapter provides that the addition of shell particles improves the mechanical properties of neat epoxy, irrespective of the percentage weight of the reinforcement. It also revealed that composites and hybrid composites' mechanical and water absorption properties varied depending on the amount of reinforcement.

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Studies on the mechanical and absorption properties of *achatina fulica snail* and eggshells reinforced composite materials

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ABSTRACT

The present study focuses on the mechanical and absorption properties of composites reinforced by *achatina fulica snail* (S-shell) and eggshell particles (E-shell). Epoxy composites of snail and eggshell particles were prepared separately with the filler content ranging from 5 to 20% by weight. Hybrid composites of both fillers were also prepared and assessed. Specimens of the composites and hybrid composites with different percentage weights of the reinforcing materials were fabricated using the resin casting method. Mechanical properties such as tensile strength, Young's modulus, impact strength, hardness and water absorption properties of the specimens were evaluated experimentally. It was observed that the addition of shell particles improves the mechanical properties of neat epoxy irrespective of the percentage weight of the reinforcement. The mechanical and water absorption properties of composites and hybrid composites varied depending on the amount of the reinforcement. Significantly, hybrid reinforcement by S-shell and E-shell particles offered superior properties in most cases. High percentage weight of calcium carbonate in these naturally sourced fillers and the synergistic effect of the S-shell and E-shells particle fillers can be attributed to high strength, stiffness, and decrease in water uptake of the composites.

1. Introduction

Development of new materials with improved properties for specific applications is mostly done by the process of combining different materials to obtain a composite material [1]. This is because composites are not found in nature directly, but they can be developed through materials engineering [2–4]. The final product obtained by combining two or more material constituents with different properties is often used to design lightweight structures with superior stiffness and strength properties. Composite material constituent with the aforementioned properties is tailored for specific applications where reduced weight, higher strength, and increased load-carrying capacity are required [5]. It is well known that the main component of a composite is the polymeric material such as epoxy, which serves as a binder. This binder holds other additives such as the fiber or the filler together to form a composite and help to maintain composite structural wholeness.

The matrix material imparts rigidity to the composite by aiding reinforcement strength to withstand high tensile loads [6,7]. However, the contribution of polymer matrices to stiffness and strength is limited due to the fact that they are soft, brittle in nature and have a limited load-carrying capacity. Several studies [8–12], have been conducted to develop a composite system with a viable support structure that possesses high load support capacity. The findings from these studies proved that the addition of carbon-based fillers has the potential to improve the properties of composites.

Moreover, studies have shown that the incorporation of organic or inorganic fillers into composite may not only provide solutions to fiber-reinforced composite failure challenges but may also be an effective way to improve the mechanical strength and stiffness of the materials [5,13,14]. However, the effectiveness of the filler material on composite properties mostly depends on the inherent properties, volume content, and its distribution within the matrix [14]. Dittanet and Pearson [15] confirmed that the addition of a filler or fillers is an active way of improving the bonding system of composite, which often results in higher strength and better moisture absorption properties. Furthermore, the use of a filler in composites has been identified as a way of reducing the cost of expensive binders which consequently reduces the cost of production [5,14,16–18]. This fact consequently led to rigorous studies on carbon based filled composite materials.

Several studies have used a variety of synthetic fillers to reinforce the matrix. This included but not limited to SiO_2, TiO_2, carbon-based fillers (carbon nanotubes and nongraphite) and calcium carbonate

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($CaCO_3$) [9,18–20]. In recent decades, natural fillers extracted from plants, hair as well as animal shells are used to improve the thermo-mechanical and physical properties of polymeric materials [21]. However, the addition of these naturally sourced materials enhances some properties and negatively affect others. However, among all the fillers, calcium carbonate ($CaCO_3$) based filler is preferred and extensively used due to its higher mechanical strength, thermal properties and accessibility at little or no cost [22–24]. Studies confirmed the effectiveness of adding synthetic fillers such as nanoclay as a feasible way of improving the composite properties [25,26]. However, nanoclay is expensive compared to naturally sourced fillers. Furthermore, it has been discovered that nanoclays contain toxic elements that can have negative effects on human health [27].

This consequently led to a growing need to produce a more environmentally friendly reinforcing material in recent decades. The search for a more suitable material with a high concentration of calcium carbonate ($CaCO_3$) led to the discovery of several shells and animal bones. These include but not limited to eggshells, mollusk shells and periwinkle.

These shells, especially eggshells were investigated and it was found to have a potential property which may be used as a filler because it contains a high content of calcium carbonate (~95% $CaCO_3$). It was suggested that they can be used as an alternative to commercial $CaCO_3$ fillers mentioned above [28–30]. Research work has been conducted on mollusk shell, animal bone and eggshell materials to determine the content of $CaCO_3$ in these naturally sourced materials. The results from these studies confirmed that these naturally sourced materials possess adequate filler characteristics suitable for use in different applications [21,31]. Furthermore, research has shown that both freshwater and land snail shell has a high content of $CaCO_3$, and the use of shells at different particle sizes has been confirmed to be an effective way of improving some properties of polymeric materials [21,31,32].

Nwanenyi et al. [33] conducted an investigation on the effect of using periwinkle shells at different particle sizes (75 µm, 125 µm, and 150 µm) and filler contents (0–30% by weight). A significant improvement in the mechanical properties with a corresponding increase in the filler content was observed. However, this study was limited to using polypropylene, thermoplastic materials and compressive molding process method in which homogenous dispersion of grains in a polymeric material may not be achieved. Furthermore, there is limited available literature on the hybrid reinforcement effect of *achatina fulica* snail and eggshells on thermoset polymer materials.

In this study, *achatina fulica* snail and eggshells were selected as reinforcing fillers due to the sufficient $CaCO_3$ content in these bio-based materials. The objective of this study is to investigate the reinforcement effect of these shell particles on the mechanical and moisture absorption properties of thermoset polymer matrices.

2. Experimental details

2.1. Raw materials collection, preparation, and synthesis

Epoxy resin and catalyst supplied with the trade names of LR 30 and LH 30 (medium) was used as the polymer matrix. *Achatina Fulica* snail-shell and chicken-eggshell particles were collected separately before they were dry-milled. The chicken eggshells were collected in a local bakery outlet in Durban, South Africa. In order to remove impurities such as inner membrane, sands and any other dirt that may be on the shell, the collected eggshells were washed in hot water. On the other hand, achatina fulica snail-shells collected from the University KwaZulu-Natal, Westville campus soccer pitch was washed and disinfected by putting them in 5% diluted household sodium hypochlorite for seven hours. Afterward, both shells were rinsed separately with distilled water and dried in an oven at 200 °C for 20 mins to ensure absolute purity and dehydration.

The clean shells were kept at room temperature for 24 h before milling. Subsequently, the shells were dry-milled in a planetary ball mill (Retsch® PM 100) [34,35]. The grinding operation involved milling at 450 rpm for 30 min in a clockwise direction. The collected shell powder was sieved using a mechanical sieving shaker (Retsch®, AS 200 basic, Germany) to a particle size of less than 50 µm, which was later used as a filler in composites materials used for this study.

2.2. Composites and hybrid composite preparation

The composite and hybrid composite specimens were prepared using the conventional resin casting method. In order to facilitate shell particle dispersion and to reduce matrix viscosity, 100 g of epoxy resin was measured in a beaker using a Snowrex digital electronic scale with an accuracy of 0.1 g and was heated to 65 °C. Afterward, shell particles of 5–20 wt% (individual and combination of the two shell particles) were slowly added to the matrix. The combination was mixed using a mechanical stirrer at 500 rpm for one hour to ensure uniform and homogeneous dispersion of the shell particles. The mixture was taken off the stirrer and allowed to cool down naturally to room temperature. Then, the catalyst was added to the epoxy-based composites using a mix ratio of 10–30 wt%. The mix was thereafter poured into an open mold to have a composite panel. However, before pouring, the wax was applied to the inner surface of the plastic mold to enable easy removal of the composite panel after two days. Investigations for the mechanical and water absorption properties were carried out on the panels after 15 days.

2.3. Mechanical testing

Mechanical tests such as tensile, hardness and impact tests were performed on the completely cured composite panel samples after fifteen days of casting. The tensile strengths of the reinforced composites were determined according to ASTM D3039 test standard. The tests were carried out on samples using a Lloyd universal testing machine (Model 43) fitted with a 30 kN load cell. Five samples were tested at ambient temperature and the constant cross-head speed of the tests was 1.3 mm/min. The mean value of the five samples was reported in the numerical results section. Barcol impresser hardness tester, commonly used for composite materials, was used to determine the hardness property of the composite panel samples. The tests were performed according to ASTM D 2583 test standard. A standard impresser with a steel truncated cone (6.82 mm height and a tip diameter of 0.55 mm) was used at 26 °C. This intender was positioned on the surface of the composite panel and a uniform downward pressure was applied by hand to collect direct readings on a dial indicator. Twenty indentation readings were randomly collected on the sample and the mean value was considered for graphical illustrations and discussions. The impact resistance of samples was determined using a Hounsfield Balance Impact Tester (model H10-3). Tests were conducted according to ASTM D 4813 standard. Five samples were tested and the average value of five readings was considered for results and discussions.

2.4. Microstructure

Microstructural studies were conducted to study the fractural mechanism of the unfilled and shell filled composite hybrid materials under tensile stress. This test was conducted on the ZAISS ULTRA FEG-SEM emission scanning electron microscope (SEM). Prior to the investigation, samples were coated with electronic thin gold.

2.5. Water absorption

Water absorption of unfilled and shell filled composite hybrid materials was investigated to determine the rate at which they absorb water and the effect of exposure to water or moist conditions. Tests were performed in accordance with ASTM D570-98 standard test

Table 1
Characteristic and elemental composition of S-shell and E-shell.

Characteristics		S-shell	E-shell
Average particle size		≤50 nm	≤50 nm
Standard deviation		27.17	35.27
Particle shape		Irregular	Uniformly sphere
Calcium carbonate (wt%)		99.4 ± 0.1	99.69 ± 0.1
Elemental composition	*Ca*	36.71	41.31
	C	22.25	14.93
	O	40.44	43.76
Other metal oxides (wt%)		0.6 ± 0.001	0.31 ± 0.001
Density g/m^3		1.4 ± 0.01	2.66 ± 0.19

specifications. Let W_1 denote the initial weight (g) of the shell. The absorption rate was determined by measuring the initial W_1 value of the shell using a Sartorius digital electronic scale with 0.00001 g accuracy (Model BP-1108) made in Germany. The composite samples were immersed in water at room temperature for 24 h. Subsequently, the sample was removed, wiped with a dry napkin and weighed to determine the final weight W_2 of the sample. The percentage of water absorption was calculated using the following equation [29]:

$$P_w = \frac{W_2 - W_1}{W_1} \times 100$$

where P_w is the percentage of absorption. Furthermore, five samples were tested and the average value of the five samples is reported.

3. Results and discussion

Table 1 presents the characteristics and elemental composition of both S-shell and E- shell particles. The particle size was determined based on the mechanical sieving shaker used as mentioned earlier and the TEM image analyzer. It was observed that shell particles were under 50 nm as detected on TEM image analysis. This corresponds to the standard provided by the mechanical sieving shaker used. The standard deviation of 89% of volume samples for S-shell and E-shells particle sizes were within 27.17 nm and 35.27 nm, respectively. The slightly higher standard deviation of E- shells compared to that of S-shells indicates the effectiveness of ball-milling in providing fairly uniform particle sizes. These particles were further examined for energy dispersive spectroscopy (EDX) using ITEM Jeol 2100 HR (High resolution) to determine the elemental composition of the shells.

As shown in Table 1, the elemental composition of both shells includes carbon, oxygen, calcium and other metal oxides at different weight percentages. It was observed that the amount of carbon in S-shells is almost twice the carbon present in E-shells. This may suggest that S-shell is tougher and harder than E-shell. Furthermore, the weight percentages of oxygen and calcium in E-shells and S-shells are significantly high. This classifies both shells as natural materials with high volumes of $CaCO_3$ with S-shells at 99.4 wt% and E-shells at 99.69 wt% of $CaCO_3$ [36,37].

3.1. *The loading effect of S-shell and E-shell particles on mechanical properties of epoxy composites*

3.1.1. *Tensile strength*

Fig. 1 shows the variance of the tensile strength for neat and shell particle reinforced composites. The histogram shows that reinforcing with S-shells and E-shells increases the tensile strength of the matrix irrespective of the percentage of shell particles. The increase in tensile strength after reinforcement varies with the weight percentage of the shell particles. Although the loading of both shell particles improved the tensile strength of the matrix, S-shell reinforced composite is observed as having a higher tensile strength compared to E-shell reinforced composite for 5%, 10%, and 20% cases. This may be due to the large volume of carbon in S-shell, as shown in Table 1, which enhances the bonding between the matrix and the filler, resulting in a higher tensile strength [38,39]. It is noted that S-shell and E-shell reinforced hybrid composite offer higher strength values for 5 wt% and 20 wt% reinforcements.

This improvement in strength may be due to the fact that both shells are $CaCO_3$ based materials which increased the resistance of epoxy to external pulling forces. The homogeneous dispersion of the shell particles could be another reason for the improvement in strength. Additionally, the higher strength of the hybrid composite for 5% and 20% reinforcements could be due to the network structure formed due to a synergistic effect that produces a stiffer and stronger material.

The incorporation of E-shells increased the neat epoxy tensile strength with corresponding increases being up to 15 wt% – 46.19 MPa to 48.45 MPa and 51.55 MPa to 62.7 MPa. A sharp drop in strength is observed afterward at 20 wt% (53.45 MPa). This trend is slightly different as compared to the improvement of strength observed in the case of S-shell and hybrid reinforced composites. In this case, the increase in strength was observed with a corresponding increase in E-shell particles of up to 10 wt% and a decrease in strength thereafter.

A significant increase in tensile strength was observed when S-shell particles were added to the matrix. Its addition increased the strength from 46.19 MPa to 59.22 MPa to 69.05 MPa and dropped to 61 MPa at 15 wt% of S-shell particles. A similar trend was observed with the hybrid composite as strength increased from 46.19 MPa to 62.46 MPa to 69.25 MPa and dropped to 53.89 MPa at 15 wt% of particles. This performance may be attributed to a homogeneous dispersion of shell particles. The decrease in strength observed at higher weight percentages of 15 wt% and 20 wt% is likely to be due to the agglomeration of particles. This created a weakness in the interconnecting bonds between the particles and the epoxy matrix leading to a composite with high and

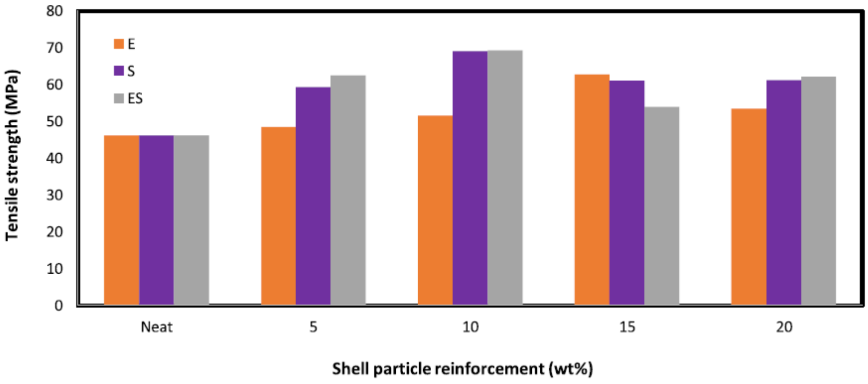

Fig. 1. Tensile strength of neat and shell particle reinforced composites.

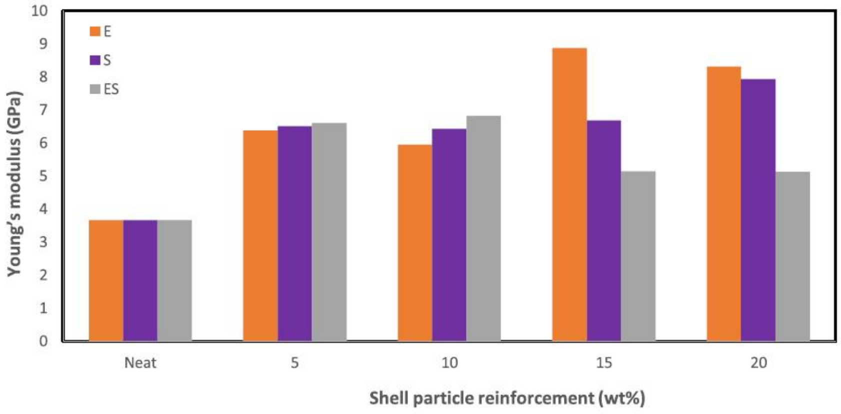

Fig. 2. . Tensile modulus of neat and shell particle reinforced composites.

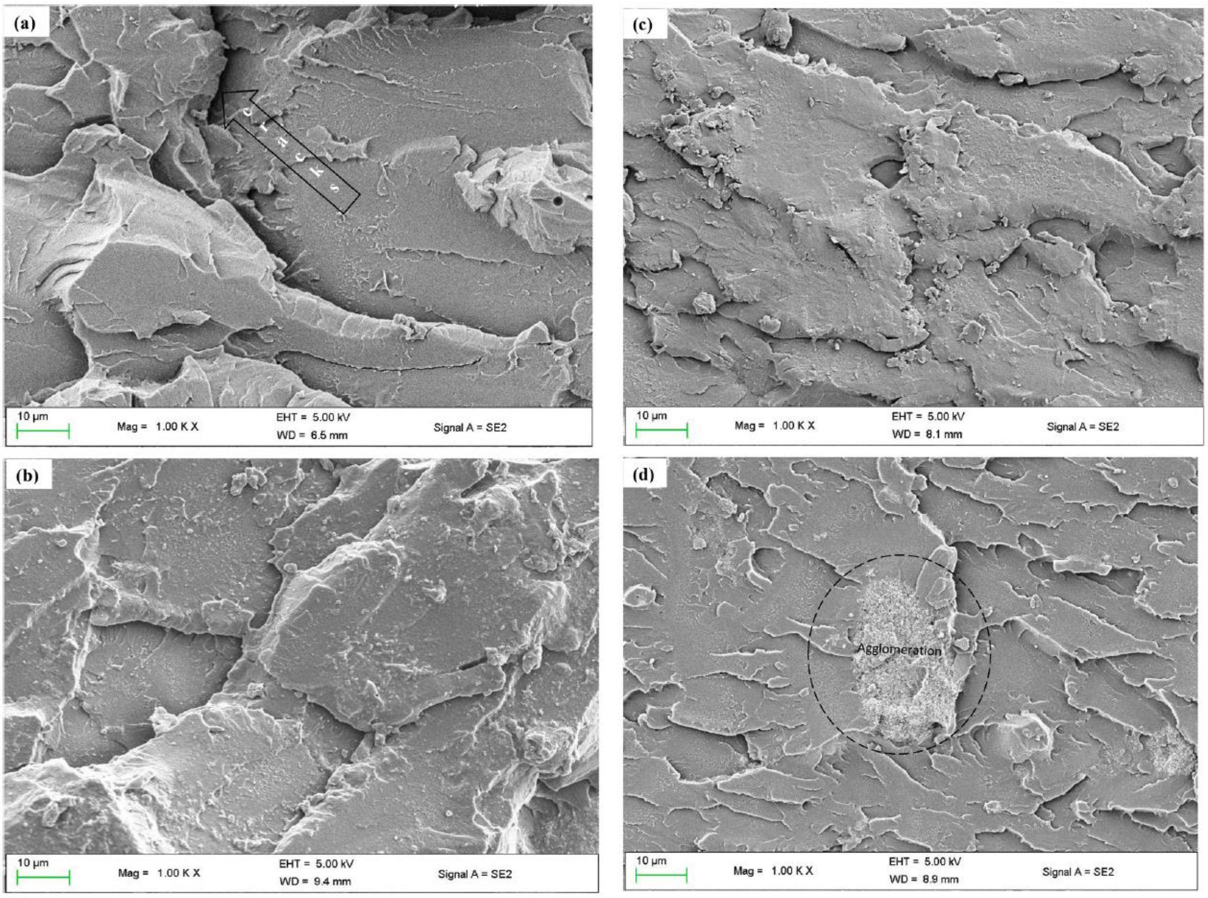

Fig. 3. SEM micrographs showing tensile fractography of; (a) Neat epoxy, (b) E 5, (c) E 10, (d) E 15, (e) E 20, (f) S 5, (g) S 10, (h) S 15, (i) S 20, (j) ES 5, (k) ES 10, (l) ES 15, and (m) ES 20 shell particle filled composites.

low filler concentrations. This, in turn, led to a decrease in toughness which affected the tensile strength of the composites.

To be precise, the addition of 5 wt% of E-shells slight improved epoxy composite strength, that is, by 4.83%, S-shell increased strength by 27.8% and hybrid reinforcement increased the tensile strength by 35.01%. At 10 wt% content, E-shells improved the strength by 11.54%, S-shells by about 49.40% and combination of both shells increased the strength by 49.84%. Despite the fact that a combination of both shells offered superior strengths at 5 wt% loading, a smaller improvement was observed at 10 wt% for S-shell and hybrid reinforcements. It can be expected that stronger S-shell characteristics dominate E-shell when combined. This may be due to a high volume of carbon in S-shell which produces a tougher and stronger structure. Additionally, uniform particle shapes and sizes of S-shell may be another reason for an increase in the tensile strength [40].

Fig. 2 shows the tensile modulus of the neat matrix and the

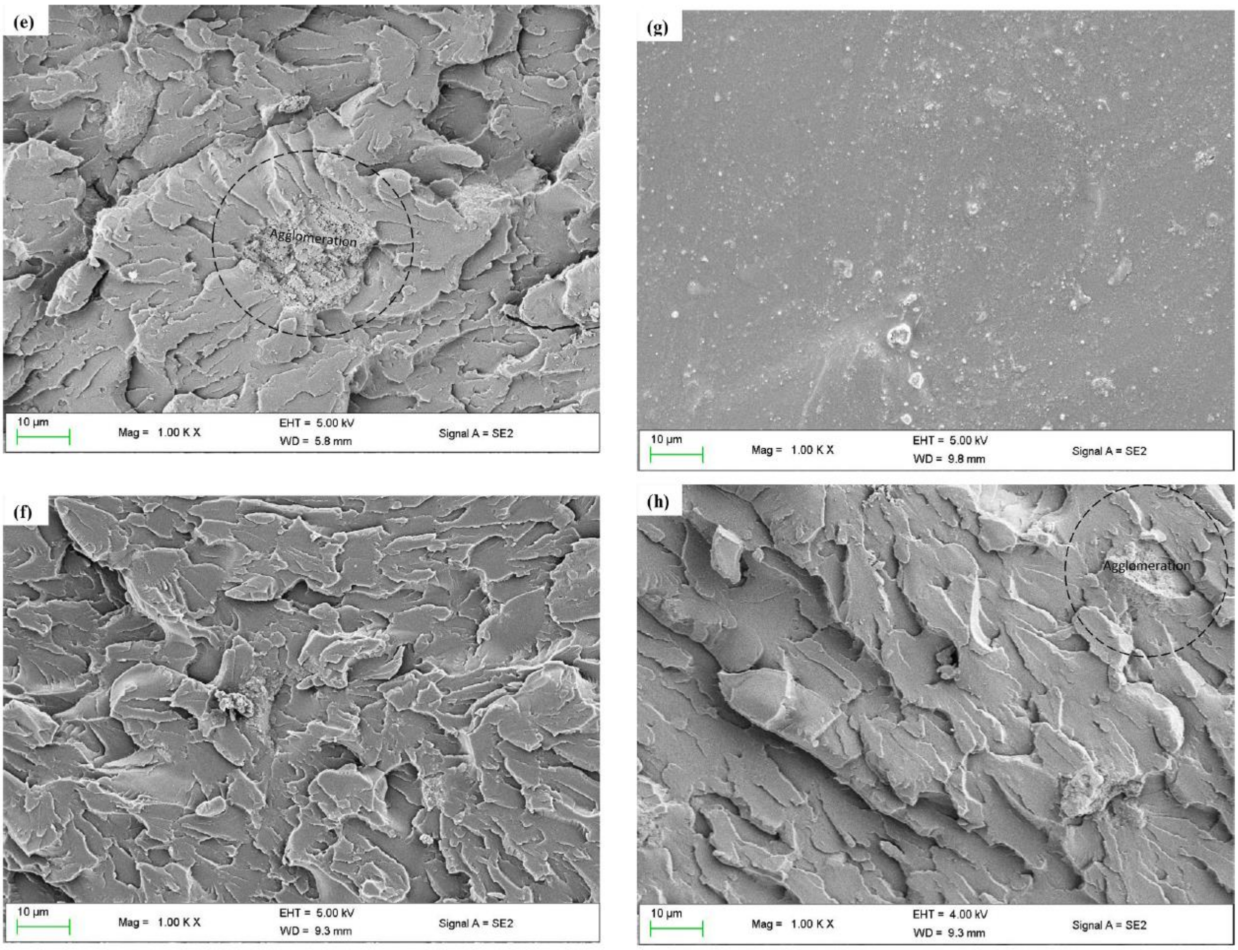

Fig. 3. (*continued*)

reinforced composites. The graph indicates that reinforcements by S-shell and E-shell particles not only increase the strength but also the stiffness. It was observed that the incorporation of the shell fillers increased Young's modulus regardless of the weight percentage. The increase may be attributed to interconnectivity formed by the particles leading to a stiffer material. The higher stiffness with S-shell reinforcement of 15% and 20% could be due to the high content of carbon present in the S-shell. In the case of E-shell particle reinforcements, an increase in stiffness was not proportional to the amount of the reinforcement, however, a significant increase in stiffness was observed at 15 wt%. This trend was similar to the strength values shown in Fig. 1. Stiffness of the hybrid composite increased by 5% and 10 wt% reinforcements and dropped afterward. This increase was insignificant when compared to composites reinforced with only one type of shell particles.

Next, the fracture surface of the neat epoxy and particle reinforced composites were examined to determine the fracture mechanisms. Fig. 3 presents the SEM images for the cases discussed above magnified at 1000 × to examine the surface structures.

Fracture mechanisms such as crack and relatively smooth plateaus can be clearly seen on a neat epoxy fracture surface in Fig. 3(a) which indicates a brittle fracture. Meanwhile, a tougher fracture surface of different layer with homogeneous distribution of grain was observed on shell filled composites except in Fig. 3(d), (e), (h), (i), (j) and (m) where shell particles agglomerated and protruded cracks formed due high-stress concentrations in that area. It is known that reinforcement by fillers often affects the polymer structures either negatively or positively depending on the filler contents. Accordingly, the incorporation of particles changes the structural formation of the matrix. Significantly, it was observed that epoxy filled with shell particles from 5 wt% to 10 wt% shown in Fig. 3(b), (c), (f), (d), (j) and (k) presented a close compact structure and relatively smooth plateaus with no cracks. This suggests compatibility and good adhesion of matrix-shell particles at the interface. This indicates that the addition of shell particles possibly introduced an incused crack arresting and pinning mechanism into the matrix at the initial stage which served as a barrier for crack propagation, resulting in increased strength, impact stress resistance and low water intake behaviors. Furthermore, agglomeration of particles and microcracks was observed on the fracture surface of 15 wt% to 20 wt% shell filled composites as seen in Fig. 3(d), (e), (h), (i), (j) and (m). The agglomeration and microcracks may be a result of having a limited amount of epoxy at grain interfaces due to the larger amount of shell particles. In this case, the higher amounts of particles induce stress concentrations which, in turn, weakens the adhesion between particles and the matrix leading to crack propagation and causing a decrease in strength.

3.1.2. Hardness properties

Hardness values for unfilled and particle-filled epoxy composites are shown in Fig. 4. It is observed that reinforcement by shell particles improves the hardness of the epoxy irrespective of weight percentages. It further noticed that the hardness properties of reinforced composites improve with an increasing weight content of the fillers.

A linear increase in hardness is distinguished as the weight content

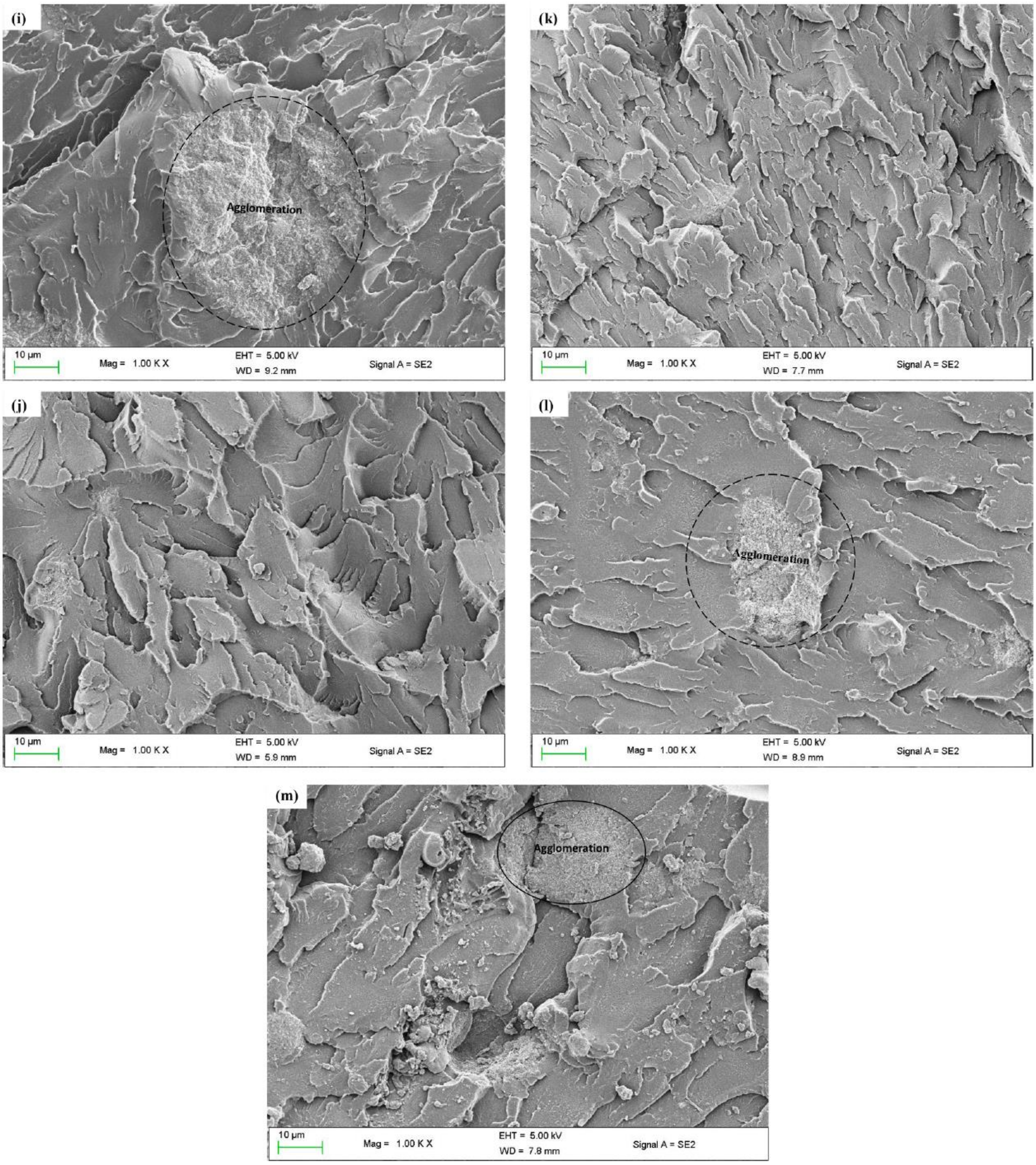

Fig. 3. (*continued*)

of shells particles increases. However, it is noted that E-shell particles increase the hardness by a very small. Improvement in hardness is due to S-shell and hybrid reinforcements are more substantial with the hybrid composite offering higher hardness values.

3.1.3. Impact properties

The impact strength values for neat epoxy and reinforced epoxy composites are shown in Fig. 5. Enhancement in strength is observed for shell particles with up to 10 wt% before a drop in the impact resistance at 15 wt% and 20 wt%.

The addition of shell particles improves the impact properties of epoxy at 5% and 10% weight contents followed by a drop at 15% and 20% contents. In the case of hybrid composite, impact strength increases by 34.99% and 43.33% at 5 wt% and 10 wt% contents, respectively. The increase in impact strength can be attributed to a uniform dispersion of shell particles forming an interconnecting bond which improves the energy-absorbing capacity of the composite. Drop in the impact strength for higher weight contents could be as a result of agglomeration caused by higher weight percentages.

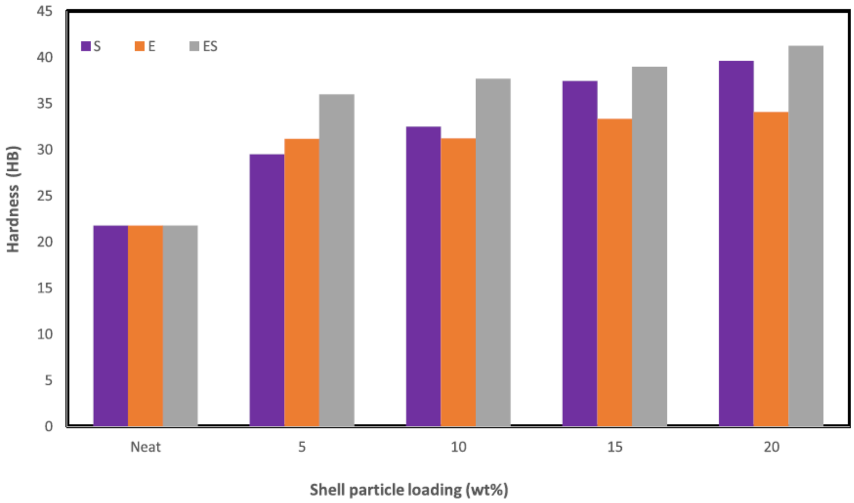

Fig. 4. Hardness properties of unfilled and shell particle-filled epoxy composites.

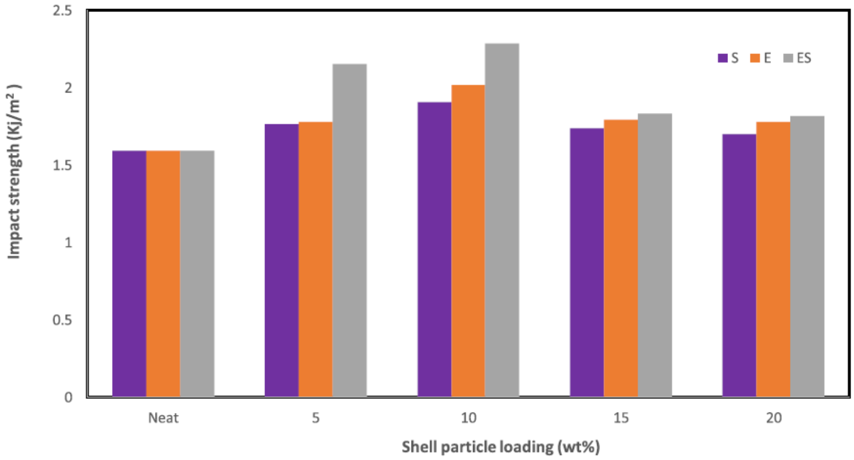

Fig. 5. Impact strength of neat and particle reinforced composites.

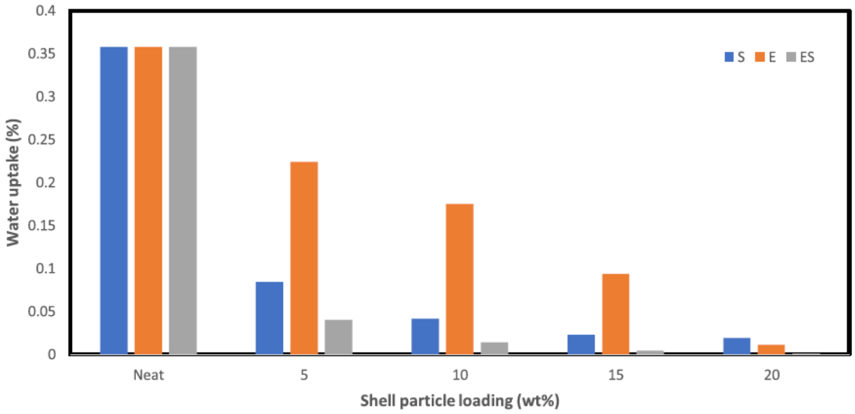

Fig. 6. Water uptake of neat and particle reinforced composites.

3.1.4. *Water uptake*

Fig. 6 presents the results for the water absorption of neat and reinforced epoxy composites. It is observed that increasing particle reinforcement decreases the water uptake substantially. This significant reduction may be due to the hydrophobic nature of the shell particles, and the interconnecting bonds formed by the fillers.

The water absorption rate varies with different fillers and the amount of loading. It is further observed that moisture absorption of the composites decreases with increasing particle content. The addition of E-shell particles reduces the water uptake of epoxy from 0.36% to

0.22% to 0.18% to 0.094% to 0.02% at weight contents between 0% and 20%. Furthermore, the addition of S-shell particles reduces the water absorption from 0.36% to 0.08% to 0.04% to 0.02% to 0.011%. Thus S-shell particles reduce the rate of water absorption better than E-shell particles. The decrease in the rate was approximately 81%, 78%, 79% and 45% at loading range from 5 to 20 %. This property could be attributed to the relatively high content of carbon in S-shells. However, the hybrid composite offered the lowest moisture sorption rate. The addition of S-shell particles reduced the moisture uptake rate by 88%, 96%, 98.8% and 99.7% as the weight content of the particles increased from 5% to 20%. The decrease in the water absorption rate may have resulted from the closer packing and homogenous dispersion of the shell particles, resulting in a stronger binding that resists water penetration.

Comparing this with the water absorption rate of composite filled S-shell particles, the addition of both S-shell and E-shell particles led to absorption rates which are 52%, 66%, 82%, and 95% lower. This may be due to the synergistic effect of calcium carbonate-based fillers which leads to a material with better barrier properties. The closer packing and homogenous dispersion of the shell particles, resulting in a stronger binding complement the improved mechanical properties reported in Figs. 1, 2, 4 and 5.

4. Conclusions

The mechanical properties and water uptake of S-shell and E-shell particle reinforced epoxy composites were investigated. High-speed (450 RPM) balling milling machine was used to process S-shells and E-shells to particle sizes of less than 50 nm. Shell particle-filled composites were fabricated using a conventional resin casting method. As expected the particle reinforced composites show improved properties as compared to the neat epoxy. Improvement in the tensile strength with reinforcements of 5 wt% and 10 wt% was noted. Similar trends were observed for stiffness property (Fig. 2), however, hybrid composite with 10 wt% of S-shell and E-shell reinforcement offered better stiffness. S-shells and E-shells particle reinforcements and their combinations provide substantially higher impact strength, water barrier and hardness properties. The overall findings suggest that composite materials based on S-shells and E-shells offer improved mechanical and absorption properties for 5% and 10% weight contents. A negative effect such as agglomeration and weak adhesion at matrix and particle interface was observed at higher contents of shells particles causing a drop in the properties compared to lower percentage reinforcements.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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THE INVESTIGATION OF THE REINFORCEMENT PROPERTIES OF NANO- CACO3 SYNTHESIZED FROM ACHATINA FULICA SNAIL SHELL THROUGH MECHANOCHEMICAL METHODS ON EPOXY NANOCOMPOSITE.

Author contribution:

Gbadeyan O.J *conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript*

Prof. S. Adali, Prof. G. Bright, and Prof. B. Sithole *provided material and equipment used for experimenting, supervised all process, and proofread the manuscript*

The chapter is the actual representation of the paper submitted to the International Journal of Material Research

7.1 OVERVIEW

This chapter presents the reinforcement effect of loading nano-calcium carbonate synthesized from Achatina Fulica snail shell via mechanochemical procedures (discussed in chapter 5) on the mechanical and thermal properties of epoxy. The nano-calcium carbonate was synthesized by further well-milled ≤ 50 µm calcium carbonate microparticles investigated in chapter 6 to nano-size ranging from 23 to 45 nm, later used as nanoparticles for producing nanocomposite. The process used to fabricate nano-calcium carbonate-filled epoxy nanocomposites was also discussed in this chapter. It also presents the method used to determine thermal stability and degradation with mechanical properties such as tensile strength, impact strength, the hardness properties of neat epoxy, and developed nanocomposites. The results revealed that the loading of the synthesized nano-calcium carbonate improved the thermal stability and mechanical properties of neat epoxy, irrespective of percentage weight loading. Significantly, loading of *Achatina Fulica* snail shell nanoparticles increased neat epoxy tensile strength by 70%, stiffness by over 200%, impact strength by 25%, and hardness by 35%. Homogeneous dispersion and loading of nanoparticles at lower concentrations result in improved mechanical properties. These improved properties are evidence that nano- $CaCO_3$ synthesized from *Achatina Fulica* snail shell possesses suitable reinforcement properties that may be used for nanocomposite fabrication.

KEYWORDS: *Achatina Fulica* Shell, Nano-$CaCo_3$, Nanocomposite, Thermal properties, Mechanical properties.

7.2 INTRODUCTION

Reinforcements, both organic or inorganic, play significant roles in modifying specific characteristics of polymeric material [142-145]. These filler materials are incorporated to increase strength, conductivity, thermal stability, or resistance to the composite indentation. According to Dittanet and Pearson [146], filler or fillers are used to improve thermal, physical, and chemical and enhance the bonding system of the composite, which often resulted in mechanical properties improvement. Even though this filler loading helps reduce the cost of expensive polymetric matrix and binders used for composite fabrication [31, 33, 147-149], its reinforcement properties need to be validated.

Fröhlich et al. [216] investigated the role of active fillers like carbon black and silica in the rubber matrix to better understand the rubber performance and the mechanism of reinforcement. This study authenticated the reinforcement potential of carbon black loading study reported by Donnet [217] on the characterization, reinforcement effect of filler loading, and understanding the kind of filler loaded in rubber found not to be well enlightened. More research was conducted to simplify the procedure used to synthesize and characterize the fiber/filler reinforced composite, authenticating the improvement in properties and the mechanism that governs the performance.

Several filters have been explored as reinforcement in polymer composites to add values to the polymeric material properties. Developed fillers such as SiO_2, TiO_2, and carbon-based fillers include but are not limited to carbon nanotubes, graphite nanopowder, and calcium carbonate ($CaCO_3$), found to be one of the most suitable and commonly used after their reinforcement potentials have been investigated [192, 193, 217]. The abovementioned fillers are extensively used based on their suitable reinforcement properties, available and low cost [149-152, 154]. Furthermore, the influence of particle sizes and loading ratio of fillers material on polymer composite properties has been investigated extensively. Reports from these investigations show that the loading of filler at different particle sizes and volumes proved to have a different effect on composite, improving one property and negatively affecting another in some cases [218-220].

Yue et al. [220] established that the amount of filler loaded in polymer has a strong effect on the thermal properties of the polymer composite. Similarly, Mohan and Kanny [137] confirmed that nanoparticle loading is a viable way of improving the mechanical, thermal, and tribological properties of the composite. However, these studies reported only the loading of synthetic fillers (nanoclay and nano-silica) with some toxic elements that cause harm to human health and the environment [158]. The increase in consumption of synthetic filler/fillers reinforced composite raised concern towards environmental and sustainable issues, which related but not limited to the energy-intensive and unsustainable production processes of the reinforcing synthetic fibers and plastics [13, 15]. Limited recyclability and end-of-life disposal options of synthetic filler/fillers reinforced composite was also identified [4, 5].

Consequently, materials from renewable resources were considered replacement components for composite production to lighten the aforementioned challenges. Filler materials such as cellulose, shells, and bone particles are currently extracted from animal and plant stems and used as reinforcement to improve composite materials' properties [38, 42, 106, 193, 221, 222]. The experimental result reported on the extract's reinforcement potentials from agricultural waste shows that this naturally sourced filler's loading effectively improves polymer composite. However, these studies are limited to the loading of eggshell particles at microparticle sizes [163, 193, 223].

Furthermore, there is limited literature where filler material is synthesized through the mechanochemical procedure (Ball milling) as most are either produce using a blender or multipurpose grinding machine. This study synthesized nano- $CaCO_3$ from *Achatina Fulica* snail shells using mechanochemical methods. The nano- $CaCO_3$ was used to reinforce the polymer composite, and reinforcement properties of the synthesized nano- $CaCO_3$ at a different loading percentage on the epoxy resin were investigated.

7.3 EXPERIMENTAL DETAILS

7.3.1 *Raw materials collection*

Epoxy resin and catalyst supplied with LR 30 and LH 30 (medium) trade were commercially purchased from AMT composite, Durban. Nano-$CaCO_3$ synthesized from sodium hypochlorite chemical treated *Achatina Fulica* snail shell using the mechanochemical method was used as nanoparticles.

7.3.2 *Nanocomposite preparation*

Epoxy-filled nanocomposites were prepared using the conventional resin casting method. To reduce matrix viscosity and facilitate shell particle dispersion, 100 wt.% of epoxy resin was measured into the beaker using a Snowrex digital electronic scale with 0.1g, placed on an electric stove heated up to 65℃. Subsequently, 1-7 wt.% of nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell was slowly incorporated into the matrix and mixed using a mechanical stirrer at 500 RPM for one hour to ensure homogeneous dispersion of shell particles. Afterward, the nanocomposite was taking off the stirrer and allowed to cool down to room temperature. The catalyst was added to the nanocomposite at the mixing ratio of 100-30 wt% to facilitate the curing process. After the blend was poured to have a composite panel and allowed to cure for two days. However, the wax was applied to the inner surface of the plastic mold before pouring. The mechanical strength, thermal stability, and material degradation of the invented nanocomposite panel were investigated after 15days.

7.4 Mechanical testing

Mechanical tests such as tensile, hardness, and impact were performed on wholly cured composite panel samples obtained after fifteen casting days.

7.4.1 Tensile

The tensile strength and Younge Modulus of the nanocomposite were measured according to ASTM 3039 test standard. The test was carried out on samples using a Lloyd universal testing machine (Model 43) fitted with a 30 kN load cell. Five samples were tested at ambient temperature, and the constant cross-head speed of testing used was 1.3 mm/min. The mean value of the five samples was reported.

7.4.2 Hardness

Nanocomposite hardness property was determined according to ASTM D 2583 test standard using a Barcol hardness tester. The investigation was conducted by placing the Barcol intender on the surface of the nanocomposite sample panel, and a uniform downward press was applied by hand for the dial indicator to generate readings. Subsequently, readings generated were collected directly from the dial indicator. Twenty-five indentation readings were randomly collected on the sample, and the means values were used for results and discussion.

7.5 Thermal properties

Thermal stability and degradation of unfilled and nano-$CaCO_3$ filled composite were determined using the thermal Analyser (Thermal Universal V 4.5 A). The investigation was conducted under a dry nitrogen gas flow at the rate of 100 mL/min from 0^0C to 1000^0C, at a heating rate of 10 ^{0}C/min.

7.6 RESULTS AND DISCUSSION

7.6.1 *Effect of loading nano-$CaCO_3$ on tensile strength and stiffness of nanocomposites*

Tensile strength and stiffness value for the unfilled and unfilled and nano-$CaCO_3$ filled composite determined using Lloyd universal testing machine as per ASTM 3039 test standard are presented in Figure 7.1. The graph representing the tensile strength in Figure 7.1 and the tensile module in Figure 7.2 is nearly alike. This output depicts that the incorporation of nano-$CaCO_3$ increased nanocomposite strength and stiffness irrespective of the loading amount. This enhancement could be due to the uniform dispersion of nanoparticles with uniform size and shape in the matrix. Furthermore, the packing of uniform geometrical shape effect of fillers on improved tensile properties was also observed. This performance corresponds with literature where the loading of nano-$CaCO_3$ synthesized from naturally sourced resources increases strength and stiffness [42, 193, 224-226]. The addition of 1 wt. % enhanced the strength of nanocomposite by 70 %, and a drop-in strength was observed afterward. The enhancement in nanocomposite strength can be traced to the high surface area of nano-$CaCO_3$ and its adhesion to the matrix.

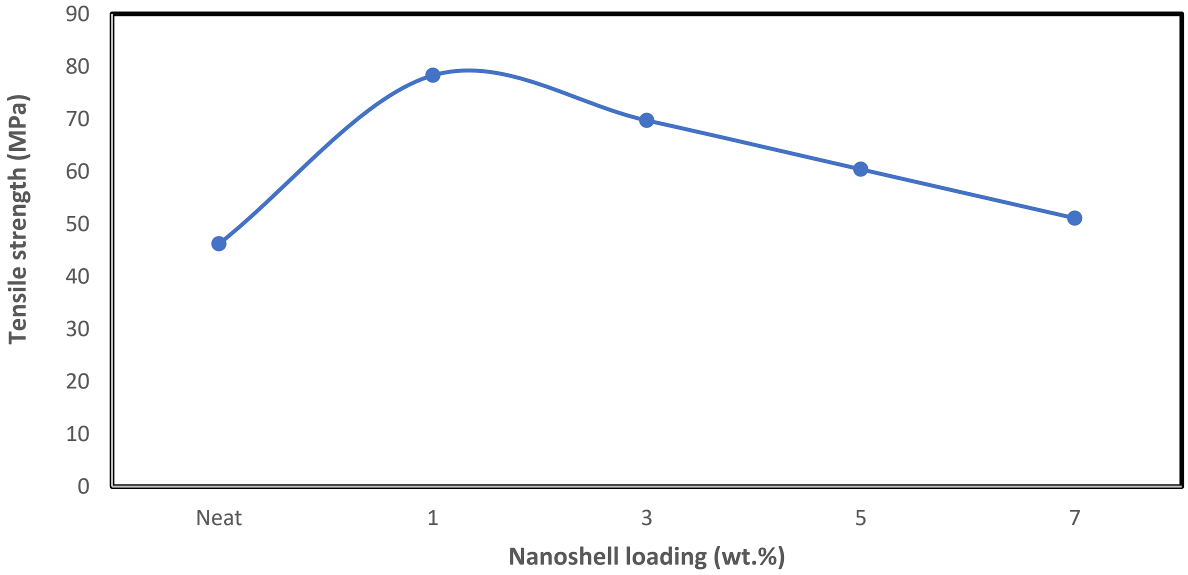


Figure 10: Tensile strength of unfilled and nano-CaCO3 filled epoxy nanocomposite.

The high surface area is often beneficial and gives room for the effective transfer of stress from the nanoparticle to the matrix, increasing the strength of the nanocomposite. This trend is consistent with literature where the effectiveness of low loading of the nanoparticle positively affects polymer composite mechanical properties [33, 218, 227]. A significant improvement in strength observed at 1 wt. % loading may also be attributed to the reinforcing effect of nano-$CaCO_3$ and the homogeneous dispersion of the incorporated nanoparticles. The chemical treatment given to the nanoparticle could be another reason for the enhancement in strength observed as the treatment remove impurity from the nano-$CaCO_3$ surface area, which eventually helps in providing strong adhesion between the nanoparticle and the matrix.

Similarly, the increase in strength of nanocomposite could be due to the compatibility of the filler and matrix, resulting in excellent adhesion at the interface of the nano-$CaCO_3$ and epoxy, producing more consistent structures that have excellent resistance to external pulling stress—the slight drop in strength seen when loading above 5 wt. % may be linked to particle agglomeration in the matrix. The addition of a large volume of particles often weakening bonds between the particles and the epoxy matrix. This influence occurred due to a limited matrix at the high filler surface area interface, which reduces stress transfer and strength of nanocomposite. The high loading of nanoparticles also creates stress concentrated in the nanocomposite, which generally induces crack propagation when exposed to external pull stress. This factor decreases toughness and stiffness, which eventually affected the tensile strength of the composites, as observed with composite filled with 7 wt. % nano-$CaCO_3$ in the

Figure 7.2 shows that the loading of synthesized nano-$CaCO_3$ enhances nanocomposite stiffness at 1 wt.% loading, and a decrease in elongation was experienced afterward. Although nanocomposite improvement varies with different loading weight percentages, incorporating nano-$CaCO_3$ improved epoxy nanocomposite stiffness regardless of loading percentage. The increase in stiffness could be attributed to the homogeneous dispersion of grain in the matrix. Reduction in stiffness observe at loading above 1 wt.% may be due to agglomeration.

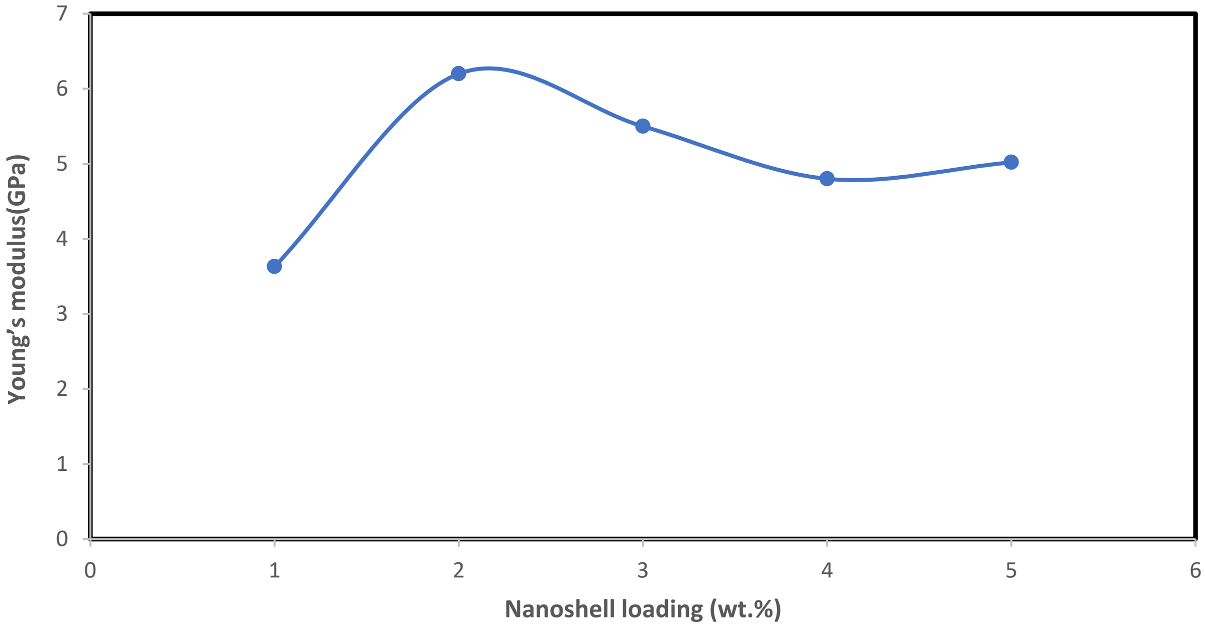


Figure 11: Tensile stiffness of unfilled and nano-CaCO3 filled epoxy nanocomposite.

The higher loading of particles often induces brittle failure due to high-stress concentrations around agglomerated particles, ultimately reducing plastic deformation [228, 229]. Meanwhile, homogeneous dispersion of nano-$CaCO_3$ and more durable matrix-filler interface structure at less loading 1 wt.% nano-$CaCO_3$ might have prevented crack instigation at the initial stage, which combats the propagation of cracks and, in turn, result in improving stiffness.

Significantly, the loading of 1 wt.% nano-$CaCO_3$ improved the stiffness of epoxy nanocomposite by 72 %, and a sharp drop in stiffness improvement was observed after that. The composite with 3 wt.%, 5 wt.%, and 7 wt.% nano-$CaCO_3$ increased epoxy stiffness by 53%, 33%, and 38 % respectively. Although all loading percentages of nano-$CaCO_3$ improved stiffness, epoxy composite filled with 1 wt.% nano-$CaCO_3$ offered superior stiffness.

7.6.2 Hardness

The hardness properties of reinforced and unreinforced epoxy nanocomposites are presented in Figure 7.3. It is observed that reinforcing with nano-$CaCO_3$ enhances the indentation resistance of the epoxy nanocomposite irrespective of the reinforcement percentages. It is noteworthy that the incorporation of

1 wt.% nano-$CaCO_3$ improved the hardness by 53%. A slight linear increase in the hardness with an increase of nano-$CaCO_3$ reinforcement was observed after this point. The enhancement in hardness can be attributed to the interlocking structure formed through an adhesion bond forming between the filler and the matrix, resulting in a stronger surface that resists indentation. These results confirm the effectiveness of nanoparticle reinforcement at low concentrations [137, 229-231].

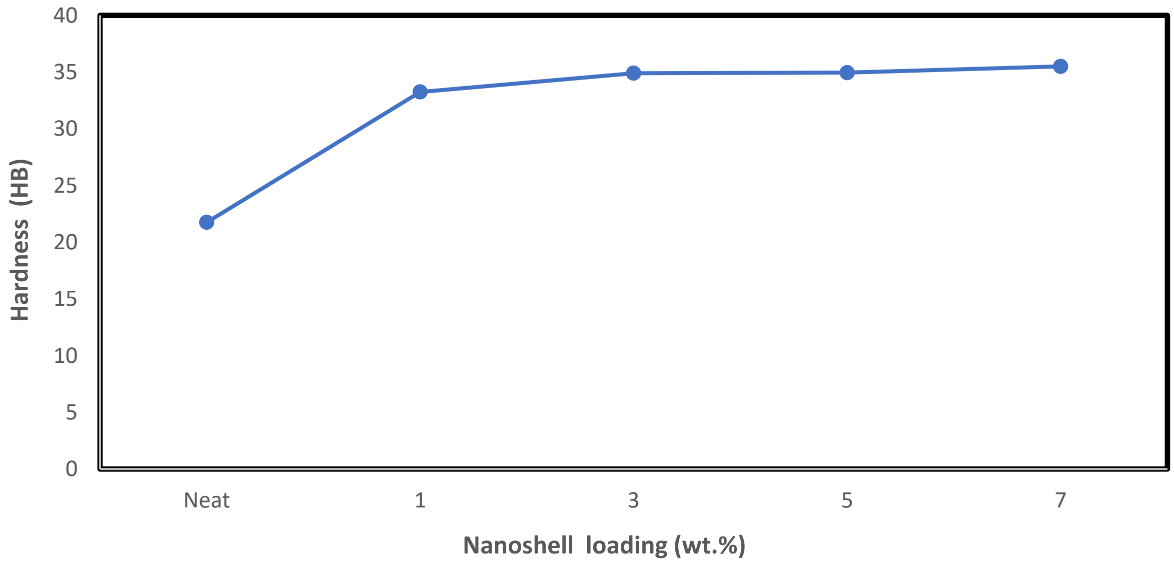


Figure 12: Hardness properties of unfilled and nano-$CaCO_3$ filled epoxy nanocomposite.

Despite the linear increase in hardness property as loading of nanoparticle increases, an insignificant improvement difference was observed after loading 1 wt.% nano-$CaCO_3$. This outcome could result from a concentrated stress area caused by a high nanoparticle loading, wearing the composite structural formulation that results in a weak indentation resistance.

7.6.3 Impact strength

Figure 7.4 presents the impact resistance of unfilled and nano-$CaCO_3$ filled nanocomposite. It was observed that the loading of nano-$CaCO_3$ increased the shock resistance of the pure epoxy composite. Significantly, loading of 1 wt.% nano-$CaCO_3$ increased impact strength by 25 %, and drop-in impact strength was observed afterward. The increase in impact strength can be ascribed to even dispersion of shell particles forming an interconnecting bond, which advances the energy-absorbing capacity of the nanocomposite. The decrease in the impact resistance observed for composite with a high loading of nano-$CaCO_3$ could result from agglomeration produced by higher weight percentages.

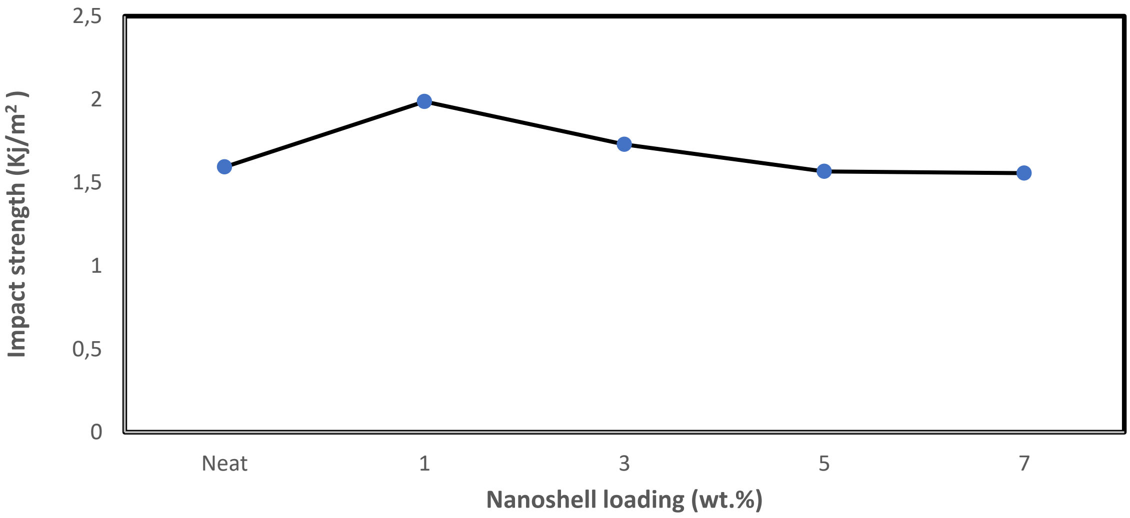


Figure 13: Impact strength of unfilled and nano-CaCO3 filled epoxy nanocomposite.

The improvement of impact strength with 1 wt.% nano-$CaCO_3$ corresponded with what was observed in Figures 7.1, 7.2, and 7.3. This inclination implies that the loading of novel nano-$CaCO_3$ synthesized from the *Achatina Fulica* snail shell at the lowest concentration is a viable way of improving the mechanical properties of the polymer composite.

7.6.4 Thermal Properties

Thermal properties in thermal stability and degradation of unfilled and nano-CaCO3 filled composite were shown in Figure 7.5. It was observed that the loading of nano-$CaCO_3$ enhanced the thermal stability and degradation temperature of the neat epoxy. An insignificant weight loss (0.057) of neat epoxy up to 100^{0}C corresponds to water's heat evaporation. Significantly loading of nano-$CaCO_3$ increased the nanocomposite thermal stability by 34% approximately. Pointedly, the nanocomposite decomposition temperature and thermal stability varied with different percentage loading of the nano-$CaCO_3$. This performance may be associated with the inherent thermal properties of the filler incorporated [232]. This trend is consistent with available literature where the loading of nano-$CaCO_3$ synthesized from naturally sourced materials improves composite materials' thermal properties [42, 52].

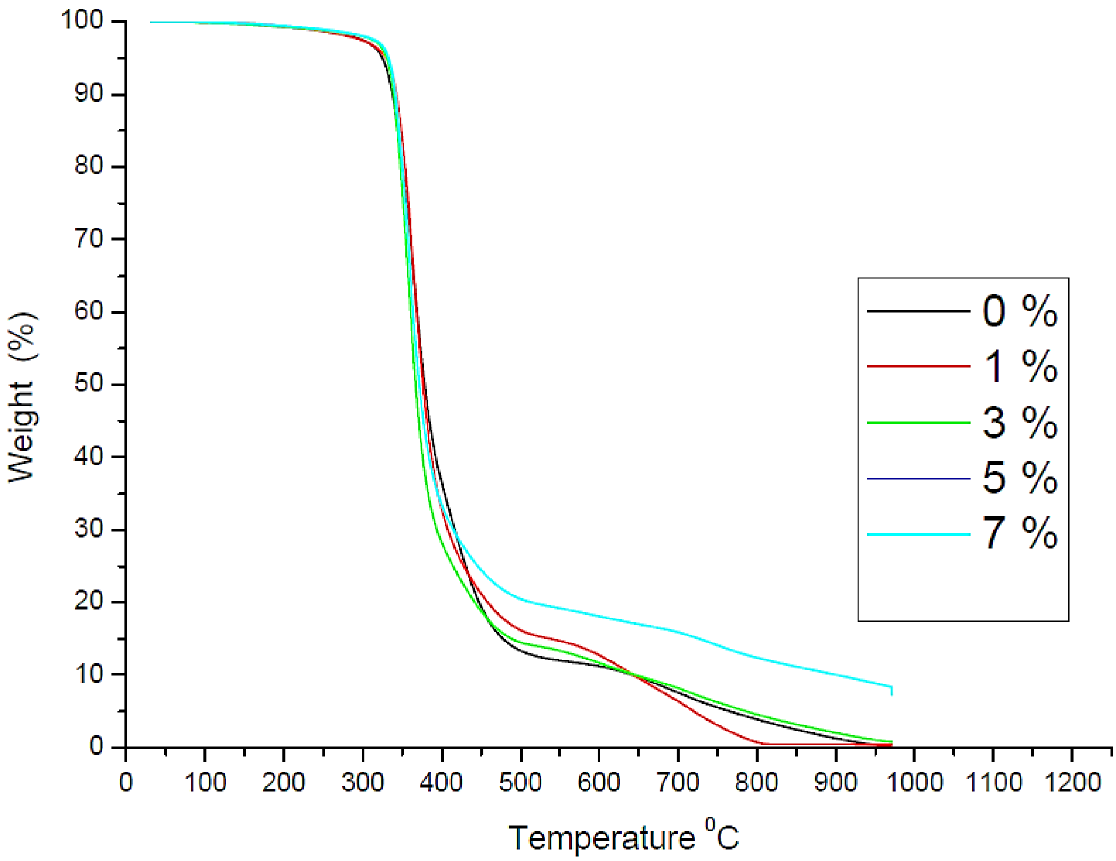


Figure 14: TGA thermogram curves of unfilled and nano-CaCO3 filled epoxy nanocomposites.

Generally, the curves show three thermal incidences within the temperature range of 0-1000^{0}C. The first phase (310-373^{0}C) is exothermic. This performance was ascribed to the breakdown of organic substances and depolymerization of hemicellulose and cleavage of glycosidic connections of cellulose [233], which eventually cause a small weight loss (up to 4.72%). The second phase (370-398 ^{0}C) is endothermic and is linked to the decomposition of calcium carbonate into carbon dioxide. The third phase (398-950 ^{0}C) represents the further endothermic decomposition of carbon dioxide to calcium oxide (ashes), which amounts to about 34% weight loss. At the second phase of decomposition temperature, unfilled composite weight loss was 86.28%. Nano-$CaCO_3$ filled composite with different loading percentages of 1 wt.%, 3 wt.%, 5 wt.%, and 7 wt.%, shows mass loss of 64.31 %, 62.23 %, 60.75 %, and 52.14 %. This output is evidence that the loading of nano-$CaCO_3$ reduces the mass loss of unfilled composite. To be specific, the maximum loading of 7 wt.% of nano-$CaCO_3$ reduced the mass loss of the unfilled composite by 40%. This outcome corresponds with the result reported by Mohan and Kanny [42], where loading of nano-$CaCO_3$ improved thermal properties.

7.7 SUMMARY

The reinforcement effect of different loading (1 wt% -7 wt%) of novel nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell on polymer composite has been successfully investigated. The nano-$CaCO_3$ was synthesized from *Achatina Fulica* snail shell using ball milling mechanochemical technique, and composite with different loading of nano-$CaCO_3$ ranges from 1 wt% to 7 wt% was developed using resin casting procedures. Thermal and mechanical properties of unfilled and nano-$CaCO_3$ filled nanocomposite were studied intensively. An increase in tensile strength, stiffness, hardness, and impact strength of nano-$CaCO_3$ filled nanocomposite was observed at 1 wt% loading. This performance was attributed to homogeneous dispersion, the high surface area of nano-$CaCO_3$ that enables stress transfer of the reinforcement, and excellent adhesion between nanofiller and the matrix, which formed a structure that offered improved mechanical properties. A decrease in mechanical properties was observed with nanocomposite with loading nano-$CaCO_3$ above 1 wt%. The decrease in performance was attributed to particle agglomeration, which induces brittle failure due to high-stress concentrations around agglomerated particles. This factor often hampers the strength and stiffness of nanocomposite.

Thermal stability and degradation of the nanocomposite were improved with a corresponding increase of nano-$CaCO_{3.}$ The decomposition temperature and thermal stability of the nanocomposite varied with different percentage loading of the nano-$CaCO_{3.}$ Thermal stability and nanocomposite degradation were improved with a corresponding increase of nano-$CaCO_{3;}$ however, nanocomposite filled with 7 wt% offered superior thermal properties. This performance was attributed to the inherent thermal properties of the nano-$CaCO_3$ incorporated. The output of the study is evidence that the loading of nano-$CaCO_3$ can improve the mechanical properties of nanocomposites but enhance thermal stability and reduce the mass loss of unfilled composite. It also confirms the reinforcement effect of nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell and suggests this material as an alternative to commercial nano-$CaCO_{3.}$

Besides, comparing the properties exhibited by nanocomposite with 1 % nano-$CaCO_3$ loading and properties exhibited by composite with 10 % loading of microparticle reported in chapter 6, nanocomposite with 1 % nano-$CaCO_3$ exhibited a slightly higher mechanical strength and stiffness than composite 10 % loading of the microparticle. Therefore, the production and usage of nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell shall more cost-effective than microparticle. In this regard, the subsequent chapter incorporates banana-fiber and nano-$CaCO_3$ with different loading percentages and later investigate the mechanical, dynamic mechanical, and microstructure properties of hybrid nano-shell plant fiber biocomposites.

7.8 RESEARCH OUTPUT

Gbadeyan O.J, S. Adali, G. Bright, and B. Sithole, "The investigation of reinforcement properties of nano-$CaCO_3$ synthesized from *Achatina Fulica* snail shell through mechanochemical methods on epoxy

nanocomposite", *Submitted to International Journal of Material Research (MR7983)*

CHAPTER EIGHT: MECHANICAL, MICROSTRUCTURE DYNAMIC MECHANICAL ANALYSIS OF HYBRID NANO-SHELL PLANT FIBER BIOCOMPOSITES

The chapter represents the actual paper submitted to the Journal of applied composite material.

Author contribution:

Gbadeyan O.J *conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript*

Prof. S. Adali, Prof. G. Bright, and Prof. B. Sithole *provided material and equipment used for experimenting, supervised all process, and proofread the manuscript*

8.1 OVERVIEW

This chapter deal with the development and investigation of a novel hybrid nano-shell plant fiber biocomposite. Nano-calcium carbonate $CaCO_3$ ranging from 1 to 5 wt% and 20 wt% banana fiber-filled hybrid biocomposite were prepared using a hand lay-up process followed by applying load on a closed mold. Nano-$CaCO_3$ of near-uniform size and shape was synthesized from *Achatina Fulica* through a mechanochemical technique. The effect of loading 30 mm fiber on the mechanical, physical, thermal properties of greenpoxy composite was investigated. The influence of nano-$CaCO_3$ loading (1 to 5 wt%) on banana fiber-filled greenpoxy composite, dynamic mechanical properties, tensile, flexural, impact strength was further investigated. The result showed that the loading of banana fiber improved mechanical properties and negatively affected temperature dependence storage modulus, loss modulus, and tan δ. Better load carrying and stress distribution capacity of the fiber within the biocomposites can be attributed to the high strength and stiffness observed for these series. The poor thermal properties of banana fiber can be ascribed to a decrease in temperature dependence properties. The loading of nano-$CaCO_3$ improved most of the banana filled greenpoxy biocomposite, and hybrid composite with 2wt% nano-$CaCO_3$ offered superior properties. Uniform dispersion, excellent matrix/ nano-$CaCO_3$/banana fiber adhesion provided a strong structure, resulting in improved mechanical and temperature-dependant properties.

KEYWORDS: *Achatina Fulica* Shell, Banana fiber, Nano-$CaCo_3$, Biocomposite, thermal properties, Mechanical properties.

8.2 INTRODUCTION

The intensification of environmental awareness, ecological concerns, and new legislation in recent decades increased global attention on the development of bio-fiber-reinforced plastic composites [20, 78, 133, 139, 234]. Biocomposite materials, developed from a combination of matrix and reinforcement of natural fibers such as banana, jute, and coir, have significant advantages over synthetic-based composite [15] [5, 16]. Advantages of composites reinforced with natural fibers include but are not limited to developing materials which are low-cost, low-density, and eco-friendly. Moreover, the high specific properties of these materials make them one of the most suitable materials for potential applications in automotive, mass transit, and marine industries [235-237]. Correspondingly, composite materials based on renewable agricultural waste are gradually employed in the industries mentioned above, as these products significantly offset the disadvantages of fossil fuels and conventional petroleum-based materials [238].

Additionally, the use of low-cost fibers has been considered an alternative way to develop biocomposites to meet people's daily needs [239]. The bio-based composites are also used in as diverse fields as sports equipment, household furniture, textile, flooring, and lightweight car components [236, 240]. Even though several efforts are directed to developing biocomposite materials with enhanced performance for several applications, the plant stem regarded as waste is still being utilized [236]. In particular, banana fiber, known as lignocellulosic fiber, obtained from the banana plant's pseudo-stem (Musa sepientum), has relatively good mechanical properties [241]. This fact has generated numerous studies, and the experimental results obtained from investigations confirmed that banana fiber offers suitable reinforcement properties for improving the mechanical strength of polymer composites [91-94].

Since composite combines two or more materials, another material needs to be combined with banana fibers to achieve a biocomposite formulation and structure. Polymeric materials, either synthetic or naturally sourced, have been used as a binder material for combining several strands of fibers to produce a composite. Banana fibers were commonly used as chopped strands, often incorporated to enhance the strength of polymeric materials. The critical lengths of fibers and the fiber volume contents are essential factors in determining the load-bearing capacity of composites. Several studies have incorporated different quantities in terms of weight percentages of banana fibers into the polymeric materials to produce composite materials with improved mechanical and thermal properties [133, 240, 242-244]. Ramesh et al. [139] processed and evaluated the mechanical properties of banana fiber reinforced polymer composites with a fiber volume content of 40-60% and compared the results with glass fiber reinforced composites with a fibre content of 50% by volume. The experimental results showed that composite materials with 50% banana fiber and 50% epoxy exhibited an excellent load-carrying capacity than other fibers/epoxy combinations. It was further suggested that the banana fibers might be used as an alternate material for conventional fiber-reinforced polymers, which may be the choice of material for the interior parts of vehicles, including aircraft interiors.

In the research work reported by Joseph et al. [245], the mechanical properties of glass fiber and banana fiber reinforced phenol-formaldehyde composites were determined and compared. The optimum fiber length for higher tensile strengths of glass fibers and banana fibers was achieved at 40 mm and 30 mm, respectively. Significant increases of up to 400 % and 320% were observed in the tensile strength and stiffness, respectively, compared to the corresponding values for neat resin with a 48% volume content of banana fibers. In like manner, Paul et al. [79] prepared and characterized a biocomposite derived from the banana plant stem. The biocomposites were fabricated with fiber reinforcements ranging from 20% to 50%, and the maximum values of mechanical and thermal properties were observed at banana fiber volume contents of 30% with a standard banana fiber size of 30 mm. Given the information provided above, it could be concluded that the reinforcements using banana fibers effectively enhance the properties of composite materials. However, the studies differ on the optimum volume contents of the reinforcements with respect to achieving higher strength and stiffness. Inconsistences in the experimental results may be due to high amounts of natural fibers used to reinforce matrix materials. For example, the amount of matrix available at the fiber interface could be limited, leading to weak bonding, resulting in poor mechanical properties [219, 246]. These challenges need to be addressed and overcome to produce materials with properties comparable to conventional composite materials.

It is noted that there is a limited amount of literature on hybrid biocomposites and, in particular, on incorporating biobased nanofillers in polymers and on banana fiber-reinforced thermoset polymers. The present study indicates that these challenges can be overcome by reducing the banana fiber reinforcement percentages and introducing biobased nanoparticles and green thermosetting polymers. The information in the available literature indicates that the optimal percentage of banana fibers has not been determined so far as there is no uniform effect of banana fiber reinforcement on composite materials at a given percentage weight. Some authors reported that composites with 30% banana fiber content exhibited superior mechanical properties in one study [79], and in another study, it was stated that 40% by volume reinforcement with a constant fiber critical length of 30mm provides superior properties [245]. The present study develops a novel nano-shell, and plant-fiber reinforced greenpoxy hybrid biocomposite by reducing the amount of reinforcement of 30 mm banana fibers to 20% and incorporating different reinforcement percentages of nano-calcium carbonate synthesized from *Anchantina Fulica* snail shell. The effect of the volume of the reinforcements for banana fiber-filled biocomposite was investigated against static, dynamic and thermal properties.

8.3 EXPERIMENTAL DETAILS

8.3.1 Raw materials collection, preparation, and synthesis

Bio-based *GreenPoxy and* catalyst supplied with the trade name of SR 33 and SD 4775 were used as a binder. The *GreenPoxy* resin is produced with a high content of carbon from plant origin. An in-house synthesizing nano-$CaCO_3$ from *Achatina Fulica* shell through mechanochemical techniques was used as a nanofiller. The nanoparticle particle size used for the study ranges from 25 nm to 63.68 nm.

8.3.2 Preparation of biocomposites and hybrids

Biocomposite was prepared using a hand lay-up process followed by applying load using a closed mold. A uniform thickness mat was prepared from the banana fiber of uniform critical length (30 mm) and placed in an open and close mold (250 mm X 250 mm X 3 mm). The fibers were chopped to a critical length of 30 mm to provide biocomposite with loading carrying capacity, enhancing mechanical strength and stiffness. Before cutting, banana fiber was chemically treated using sodium hydroxide (NaOH) to enhance the adhesion and interfacial bonding of fiber and matrix [105-113]. The fiber was soaked in a 6% sodium hydroxide (NaOH) solution for a day, washed under running water, dried for 24 hours, and after that dry in an oven at 60℃ for 1hr to remove moisture remnants. Simultaneously, nano-$CaCO_3$ was dispersed in the *GreenPoxy* using a magnetic stirrer with a hotplate. To enable nano-$CaCO_3$ dispersion in the greenpoxy and reduce greenpoxy viscosity, 100 wt% of GreenPoxy resin was measured into the beaker using a digital electronic scale of 0.1g. The beaker was placed on a hotplate and heated up to 50℃. The temperature of the matrix in the beaker was monitored with the aid of a temperature probe. Later, nano-$CaCO_3$ (1-5 wt%) was slowly incorporated into the matrix and mixed using a mechanical stirrer at 500 rpm for one hour to ensure homogeneous dispersion.

Nano-$CaCO_3$ and *GreenPoxy* mixture was taking off the stirrer and was allowed to cool down to room temperature. Then, the catalyst was added to the biocomposite at a mixing ratio of 100-27 wt%. The releasing agent (wax) was applied to the inner surface of the mold, and the fiber mat was positioned. After that, the amalgamation was poured on the fiber mat, placed in the mold, and spread using a wooden spatula. The mold was closed, and 92 N load was applied on the mold have a composite panel and allowed to cure for two days. After 15 mins, the fiber mat was repositioned in the mold, then nano-$CaCO_3$/*GreenPoxy/*catalyst mixture was poured. The cured hybrid biocomposite was removed from the mold after 24 hours and post-cure at 80^0C for 4 hrs. The mechanical strength of the fabricated nanocomposite panel was investigated after 15days.

8.4 TESTING

8.4.1 Tensile

The tensile strength and Young's modulus of biocomposite were determined according to ASTM 3039 test standard. The test was carried out using a Lloyd universal testing machine (Model 43) fitted with a

30 kN load cell manufacture by MTS, United States of America. Tensile of 250 mm x 25 mm x3 mm, in length, width, and thickness by dimensions, were cut from the neat greenpoxy and the biocomposite laminate samples using a CNC machine. Five samples were tested at ambient temperature, and the constant cross-head speed of testing used was 0.85 mm/min. The mean value of the five samples was reported.

8.4.2 Flexural

According to ASTM, the flexural strength and stiffness of unfilled greenpoxy, banana fiber-filled greenpoxy biocomposite, and nano-CaCO3 and greenpoxy nanohybrid biocomposite were determined D790-02 standard specifications. The investigation was conducted using a Lloyd universal testing machine MTS UTM Tensile Tester (Model LPS 304 – 424708 series) manufacture by Lloyd Ltd. Bognor Regis, West Sussex, UK, fitted with a 30 kN load cell. The test technique made use of a simply supported beam of 16:1 span-to-thickness ratio, with center loading support span. The samples' span length was 48 mm, and the nominal thickness was 3 mm, while the width was maintained at 12.7 mm. Five flexural specimens were investigated, and the average values of flexural strength obtained for all five specimens were reported. The constant cross-head speed of testing used was 0.85 mm/min.

8.4.3 Hardness

The resistance to indentation (hardness property) of the hybrid biocomposite was determined using Barcol hardness tester (Shenyang TX Testing instrument, China), commonly used to determine composite materials' hardness property. The investigation was conducted according to ASTM D 2583 test standard. A standard impressed with steel truncated cone (6.82 height and a tip diameter of 0.55mm) was used at an angle of 26˚. This intender was positioned on the top-flat surface of the hybrid biocomposite panel, and a uniform downward press was applied by hand, and readings were collected directly from the dial gauge. Twenty indentation readings were randomly collected on each specimen, and the means values were used for graphical illustration and discussion.

8.4.4 Water immersion

Biocomposite was immersed in water for 24 hours at room temperature to determining the water absorption rate and the effect of exposure to water or moist conditions. This investigation was performed following ASTM D570-98 standard test specifications. Before immersion, the initial weight of five samples was taken for each biocomposite formulation, then dried in the oven at 70 ^{0}C for 2 hours to remove moisture content in the sample. The samples were collected from the oven and dipped to water at room temperature. Subsequently, the sample was removed, wiped with a dry napkin, and weighed to determine the sample's final weight (W2) using a Sartorius digital electronic scale with 0.00001g accuracy (Model BP-1108) made in Germany. The percentage of water absorption was measured using the following equation.

$$W_B = \frac{W_2 - W_1}{W_1} \times 100$$

Where W_B is the percentage of absorption. Furthermore, five samples were tested, and the average W_B The value of the five samples is reported [193].

8.4.5 Impact

According to ASTM D6110-10 at room temperature, the Charpy test was performed using an Unnotched Izod impact machine manufactured by Tensiometer Ltd., Croydon, England. Five biocomposite test specimens were investigated, and the mean value was considered for results and discussion. This investigation was conducted to determine the resistance of biocomposite to shock

8.4.6 Scanning electron microscopy

Biocomposite fracture surface sputter-coated using a Quorum K550x gold sputter coater at 25mA was observed on the Phenom Pharos Desktop SEM images captured at an accelerating voltage of 10kV; this investigation was carried to determine the fracture mechanism.

8.4.7 Dynamic mechanical analysis (DMA)

DMA measurements were carried on unfilled, banana fiber-filled biocomposite, and nano-shell and plant fiber-filled hybrid biocomposite at a frequency of 100 Hz in a 3-point bending mode (TA instruments model Q800, New Castle, DE, USA) from 20 ℃ to 200 ℃ under atmospheric conditions. This measurement determined the temperature dependant storage modulus, loss modulus, and tan δ peaks of the developed biocomposite. The specimen size of 60 mm X 12mm X 3 mm was investigated.

8.5 RESULTS AND DISCUSSION

8.51 Tensile strength and stiffness

The tensile strength and the tensile modulus of unfilled, fiber-filled biocomposite and nano-shell and plant fiber-filled hybrid biocomposite are presented in Figures 1 and 2. Figure 1 shows that the inclusion of fibers increased the tensile strength of the greenpoxy composite (control) from 73,3 MPa to 102,7 MPa, which is about an increase of 40% compared to the unreinforced case. This improvement in strength can be attributed to reinforcement properties and the load-carrying capacity of the fibers. The improvement can also be related to fiber and matrix compatibility as greenpoxy is developed from plant extract

Table 8.1: Tensile properties of unfilled, fiber-filled biocomposite, and nano-shell and plant fiber-filled hybrid biocomposite.

Biocomposite	Tensile strength, MPa	Tensile Modulus, GPa
Neat greenpoxy (Control)	73.3 ± 3.2	3.08 ± 0.31
Greenpoxy + fiber	102.7 ± 2.8	3.73 ± 0.2
Greenpoxy + fiber + 1 wt.% nano-$CaCO_3$	116.7 ± 2.6	3.8 ± 0.85
Greenpoxy + fiber + 2 wt.% nano-$CaCO_3$	180 ± 2.7	7.1 ± 0.96
Greenpoxy + fiber + 3 wt.% nano-$CaCO_3$	111 ± 2.4	4.2 ± 0.1
Greenpoxy + fiber + 4 wt.% nano-$CaCO_3$	119 ± 3.7	5.3 ± 0.29
Greenpoxy + fiber + 5 wt.% nano-$CaCO_3$	121.9 ± 2.8	4.5 ± 0.28

This finding is consistent with available literature where the inclusion of banana fibers improved tensile strength [93, 139, 235, 247]. It was further observed that the inclusion of nano-$CaCO_3$ increases the strength and stiffness of hybrid nano-shell and plant fiber-filled biocomposite, irrespective of reinforcement ratio. However, a significant linear increase in hybrid biocomposite strength and stiffness was obtained at adding nano-$CaCO_3$ up to 2 wt.%, and a reduction of this percent was seen afterward. This trend is consistent with the available literature results where a low concentration of loading nano-$CaCO_3$ synthesized from a natural source such as a shell improves biocomposite strength [42, 193, 248]. The addition of nano-$CaCO_3$ enhanced hybrid biocomposite strength from 102,7 MPa to 116,7 MPa to 180 MPa. As the loading increases from 3 wt.% to 5 wt.% nano-$CaCO_3$ loadings, composite strength decreased from 111 MPa to 119 MPa to 121,9 MPa.

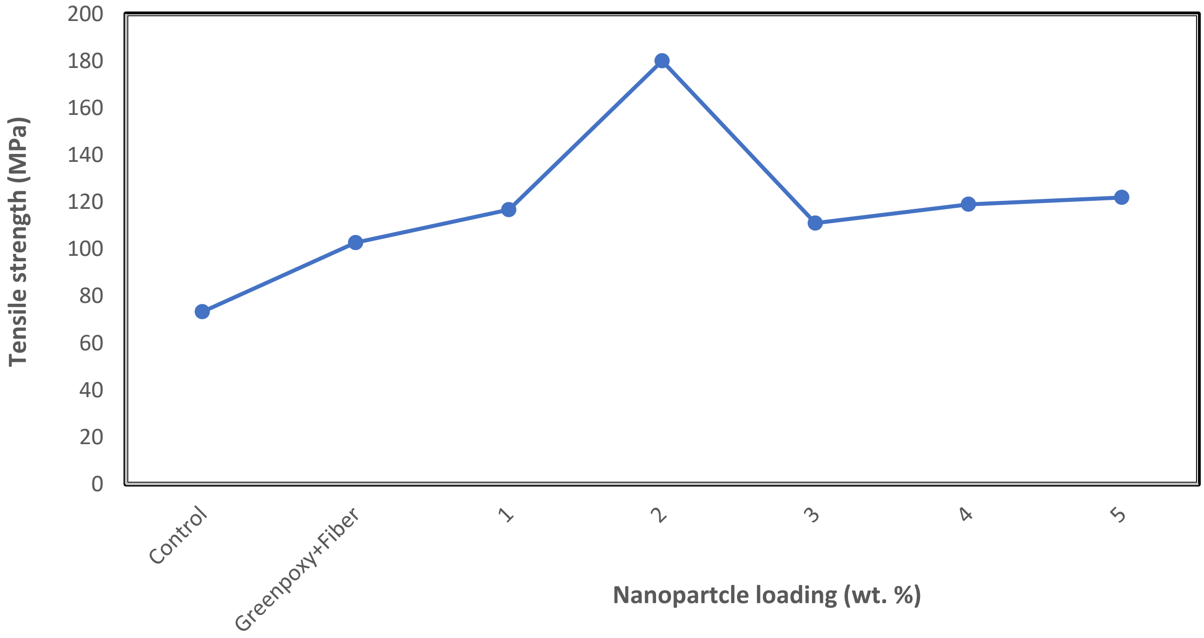


Figure 15: Graph showing tensile strength of unfilled greenpoxy, banana filled greenpoxy composite and hybrid nano-shell plant fiber biocomposite.

To be specific, the banana fiber-reinforced composite's pulling strength was improved by 13.6% and 75.3% as nano-$CaCO_3$ loading increased from 1 wt.% to 2 wt.%. As the loading of nano-$CaCO_3$ increased from 3 wt.% to 5 wt.%, the biocomposite strength increased by 8%, 15%, and 18%. This output proved that the hybrid biocomposite with a lower concentration of nano-$CaCO_3$ offered higher strength than the hybrid biocomposite with higher nanoparticle loading. This performance depicts nanoparticles' reinforcement potential at a lower concentration, allowing homogeneous dispersion of grains in a polymer composite, which eventually resulted in improved tensile strength. The loading of nanoparticle-modified hybrid biocomposite structural formation forms a synergistic interlocking effect with the incorporated fiber and matrix, producing a more robust structure with excellent resistance to external pulling forces. A sharp decrease in strength at nano-$CaCO_3$ loading above 2 wt.% may be attributed to the agglomeration of reinforcement in greenpoxy biocomposite [225]. Particle agglomerated in matrix function as a micro-level particle with lesser surface area, which eventually reduces stress transfer and load-carrying capacity. The agglomerated particle in biocomposite often affects adhesion effectiveness at the incorporated filler and fiber interface, forming a stress concentrated area contributing to decreased strength [42, 193, 248]. For the stiffness, the result represented in Figure 4 shows that the loading of banana fiber is not the only way of improving strength and an effective way of improving the toughness and stiffness of greenpoxy biocomposite. It was observed that the inclination of the graph illustrated in Figure 8.1 for tensile strength and figure 8.2 for tensile is almost matching.

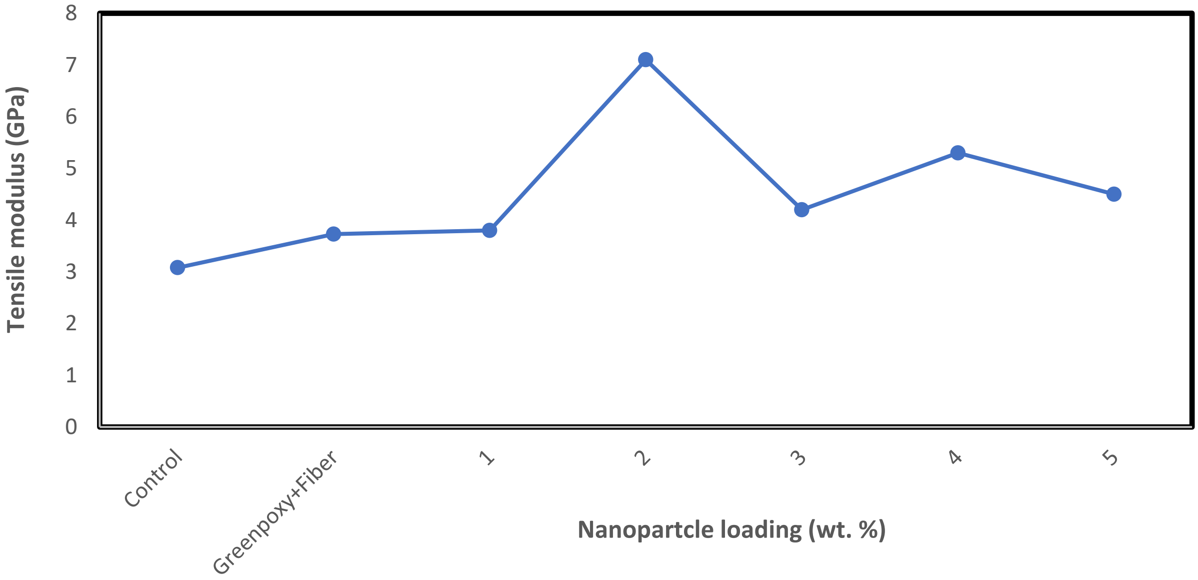
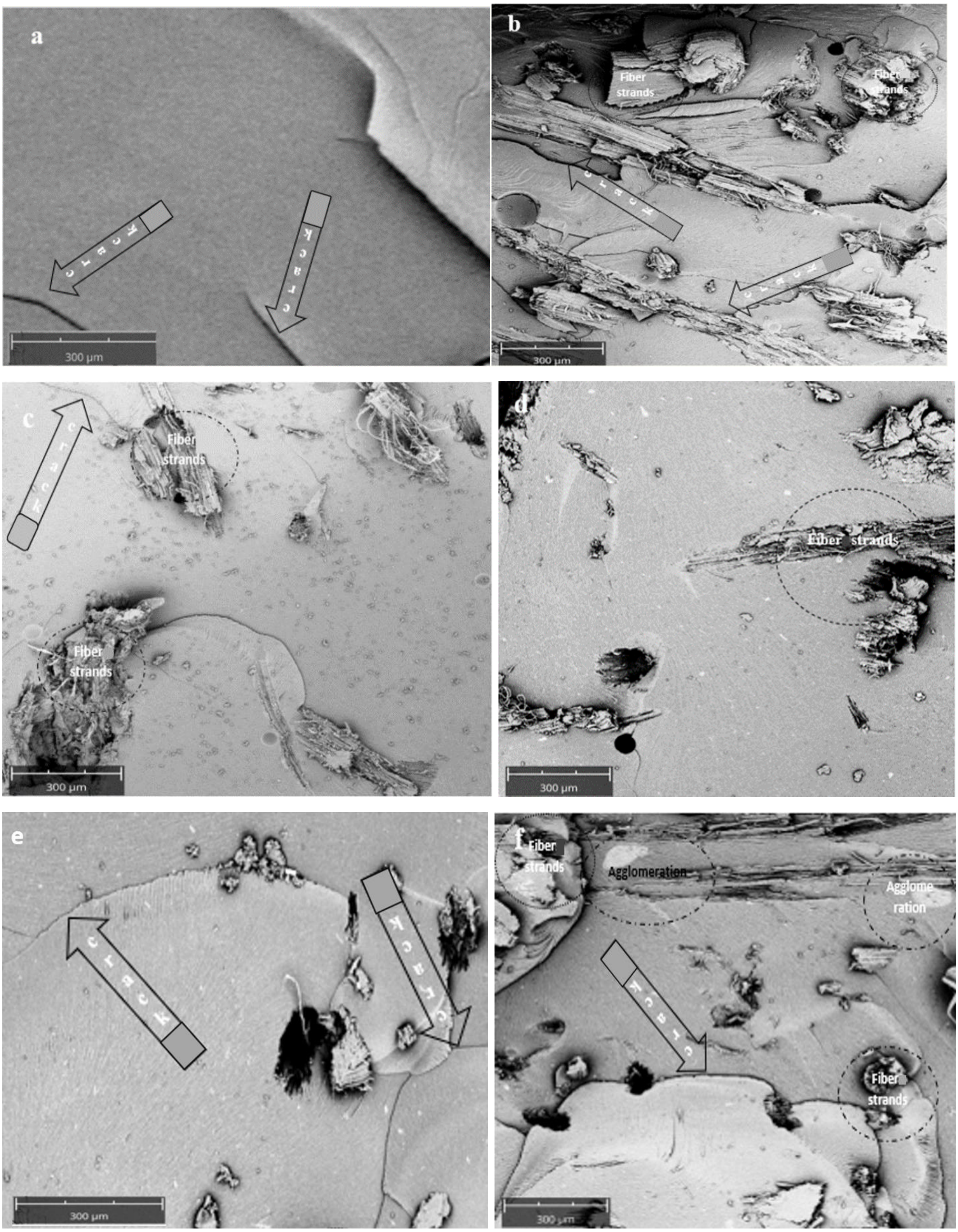


Figure 16: Graph showing tensile modulus of unfilled greenpoxy, fiber-filled biocomposite, and hybrid nano-shell and plant fiber-filled hybrid biocomposite

The modulus of banana fiber-filled greenpoxy biocomposite with nano-$CaCO_3$ loading up to 2 wt.% is higher than neat greenpoxy and banana fiber-filled greenpoxy biocomposite series with nano-$CaCO_3$ loading above to 2 wt.%. This performance showed the synergistic reaction between the fiber and nanoparticle incorporated, formed interconnectivity that provided a stiffer structure that produced a stiffer material. The alkali chemical treatment of fiber and nano-$CaCO_3$ provides superior adhesion of filler/fiber, resulted in high stiffness observed [112, 249-251]. A significant increase in stiffness of about 90% was observed with 2 wt % loading of nano-$CaCO_3$ and dropped afterward. This trend was comparable to the strength values shown in Figure 8.1. The dropped in material stiffness of hybrid biocomposite with nano-$CaCO_3$ above 2 wt % may be attributed to reinforcement agglomeration, causing a stress concentration area that aids crack propagation and reduce stiffness [248]. It is possible that up to 2 wt.% loading of nano-$CaCO_3$ serves as a resistance medium to crack propagation due to the homogenous dispersion and adhesion, which eventually improved stiffness. The high loading of nano-$CaCO_3$ may also encourage brittles failure due to stress concentration around the particle agglomerated area, reducing plastic deformation. However, the uniform dispersion and good fiber/filler/material interface adhesion of hybrid biocomposite at lower loading up to 2 wt.% may have provided pinning and induced crack arrester at the initial crack propagation stage, resulting in elongation increase.

8.5.2 Fracture mechanisms

Scanning electron microscopy was later conducted at 500X magnification to determine the fracture mechanism. Figure 8.3. shows the fracture surfaces of neat greenpoxy, fiber-filled biocomposite, and nano-shell and plant fiber-filled hybrid biocomposite. Fracture structures such as fiber breakage, tight surface with cleavages, homogeneous distribution of fiber firmly bonded with the matrix, cleavages, tougher with a relatively smooth surface, and crack structures were observed. The fracture surface of neat greenpoxy in figure (8.3a) shows relatively smooth and cleavage structures with cracks, signifying a brittle fracture. Accordingly, the incorporation of the banana fiber changes the structural formation of the matrix. Accordingly, on the fracture micrograph, incorporating the banana fiber changes the matrix's structural formation, as shown in Figure 8.3b. Homogeneous fiber distribution firmly bonded with the matrix, cleavages, tighter with a relatively smooth surface, and crack structures were observed on the micrograph of banana-filled greenpoxy. This structural formulation may be attributed to an increase in the strength of neat greenpoxy after banana fiber was incorporated. Fracture surfaces of banana-filled biocomposite with 1 wt.% and 2wt.% nano-$CaCO_3$ (Figure 8.3c and 8.3d) loading appears smoother with a uniform dispersion of nano-$CaCO_3$; however, a tiny crack was also observed on the fracture surfaces. Possibly, the small loading of nano-$CaCO_3$ at 2wt.% might have stopped the propagation of crack and avert the direction of crack propagation. The loading of nano-$CaCO_3$ might have provided an interlocking structure that induces higher strain and bears the extra load, resulting in increased strength, elongation, and reduced water uptakes of banana filled biocomposite.


a
crack
crack
300 µm
b
Fiber strands
Fiber strands
crack
crack
300 µm
c
crack
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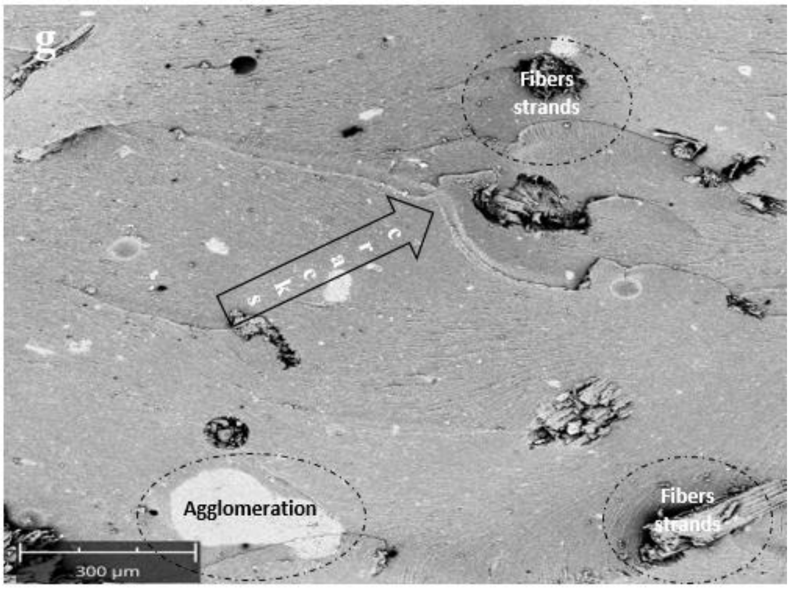


Figure 17: SEM micrographs showing tensile fractography of; (a) Neat greenpoxy, (b) Greenpoxy + fiber (c) Greenpoxy + fiber + 1 wt.% nano-$CaCO_3$ (d) Greenpoxy + fiber + 2 wt.% nano-$CaCO_3$ (e) Greenpoxy + fiber + 3 wt.% nano-$CaCO_3$ (f) Greenpoxy + fiber + 4 wt.% nano-$CaCO_3$ (g) Greenpoxy + fiber + 5 wt.% nano-$CaCO_3$ biocomposite.

Even though nano-$CaCO_3$ is included in this hybrid biocomposite series, it is challenging to see the fracture surfaces' particles, suggesting uniform nanoparticle dispersion. It was also observed that the amount of crack on fracture surfaces increased as the loading of nano-$CaCO_3$ from 3wt.% and 5wt.%. This structural formation may be attributed to a sharp drop in strength and modulus observed. These hybrid biocomposites' fracture surfaces show a degraded surface with cracks, and particle agglomeration becomes visible. Cracks initiated and propagated by particle agglomeration with a rough surface structure were seen fracture surface of hybrid composite with 5wt.%. Loading of nano-$CaCO_3$ showed in Figure 8.3g. The agglomeration and microcracks may be due to the high-loading of nano-$CaCO_3$, causing the debonding of filler/fiber/matric at the interface and reduces resistance to strain stress of the external pulling force. The agglomeration of nano-$CaCO_3$ might have offered a weaker structure with a stress-concentrated section that encourages crack propagation, harming the strength and stiffness of hybrid biocomposite.

8.5.3 Flexural strength and stiffness

The flexural strength and modulus of banana fiber-filled biocomposite and hybrid nano-shell and plant fiber-filled hybrid biocomposite are illustrated in Figures 8.4 and 8.5. Notably, the loading of banana fiber increases the strength and stiffness of neat greenpoxy composite. Many studies have reported that loading short banana fiber improves polymeric material's strength and stiffness [94, 252-254].

Table 8.2: Flexural properties of unfilled, fiber-filled biocomposite, and nano-shell and plant fiber-filled hybrid biocomposite.

Biocomposite	Flexural strength, MPa	Flexural modulus, GPa
Neat greenpoxy (Control)	22.5± 3.2	0.38 ± 0.035
Greenpoxy + fiber	32 ± 2.8	1.05± 0.017
Greenpoxy + fiber + 1 wt.% nano-$CaCO_3$	53.2 ± 2.6	1.78 ± 0.027
Greenpoxy + fiber + 2 wt.% nano-$CaCO_3$	56 ± 2.7	1.25 ± 0.011
Greenpoxy + fiber + 3 wt.% nano-$CaCO_3$	24.3 ± 2.4	0.41 ± 0.31
Greenpoxy + fiber + 4 wt.% nano-$CaCO_3$	23.5± 3.7	0.51 ± 0.022
Greenpoxy + fiber + 5 wt.% nano-$CaCO_3$	26.55 ± 2.8	0.53 ± 0.029

As shown in Table 8.2, the addition of 2 wt.% loadings of nano-$CaCO_3$ improved strength; however, superior stiffness of banana fiber-filled biocomposite was observed at 1 wt.%, and afterward, a drop-in strength was seen. This performance may be attributed to the homogeneous dispersion of small nanoparticles incorporated. Significantly, the loading of 1 wt.% nano-$CaCO_3$ increased banana fiber-filled biocomposite by 66%, and a further increase of 5.3% was observed at 2 wt.% loadings. This notable improvement depicts the effectiveness of loading nanoparticles at a lower concentration, enhancing the nanoparticle's homogenous dispersion in the matrix. The uniform dispersion helps the fillers' interfacial adhesion, forming an interlocking structure with the matrix, which improves strength and stiffness [246]—a sharp decrease in the strength of above 2 wt.% loadings.

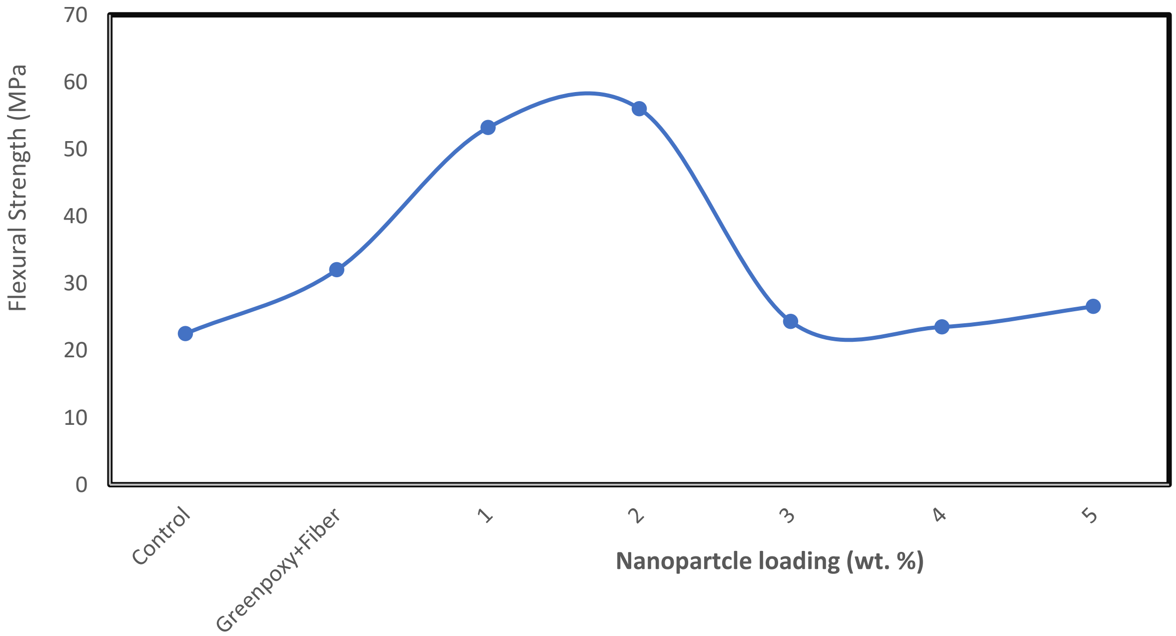


Figure 18: Graph showing flexural strength of unfilled greenpoxy, banana filled greenpoxy composite and hybrid nano-shell plant fiber biocomposite

The decrease in flexural strength of hybrid nano-shell and plant fiber-filled hybrid biocomposite after loading 2 wt.% may be due to a higher concentration of nanoparticles. Furthermore, the high loading of nanoparticles often serves at the micro-level, which reduces the filler/matrix adhesion due to the insufficient amount of matrix at fiber/fiber and matrix interface. The reduction at interface adhesion often results in a weak and brittle structure with little strength and stiffness. For modulus, loading of 1 wt.% nano-$CaCO_3$ increased stiffness of banana fiber-filled biocomposite significantly, as shown in Figure 5. The stiffness improvement may be attributed to the functional carrying capacity of the fibers, homogeneous dispersion of the nanoparticles, and the more solid interfacial adhesion form by the filler/fiber and matrix, which offered a more stable structure that prevents flexural strain.

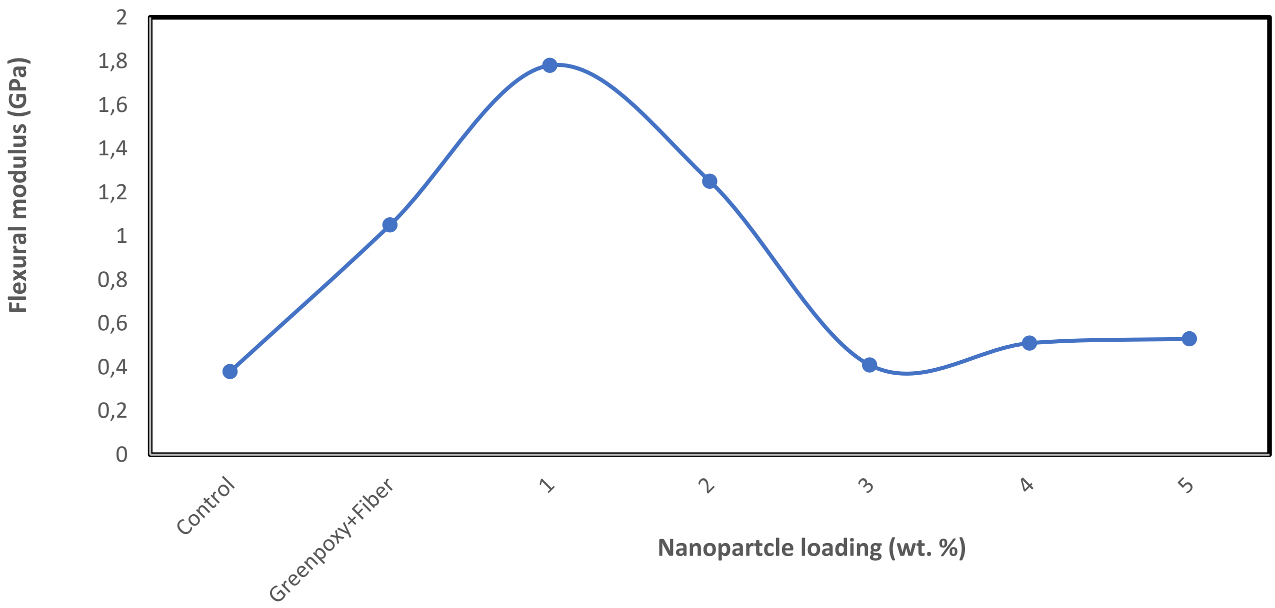


Figure 19: Graph showing flexural strength of unfilled greenpoxy, banana filled greenpoxy composite and hybrid nano-shell plant fiber biocomposite

The decrease in stiffness may be due to increased loading resulting in particle agglomeration. This kind of agglomeration regularly creates a high-stress concentration area that initiates and propagates cracks. The propagated cracks become more prominent, leading to failure when subjected to external stresses, and this can be attributed to a decrease in the strength and stiffness observed at the loading of nano-$CaCO_3$ above the 2% level.

8.5.4 Hardness

The hardness properties of unfilled greenpoxy, banana filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite shown in Figure 6. The investigation was conducted to determine biocomposite resistance to indentation. A significant increase in the hardness property of greenpoxy of about 37% was observed after incorporating the banana fiber into the matrix material. This indicates that the inclusion of banana fibers increases the surface toughness of the biocomposite. This performance indicates that the inclusion of banana fibers increases biocomposite surface toughness, which may be attributed to the superior adhesion fibers and the matrix due to the fibers' excellent wettability. It was further observed that the reinforcement with nano-$CaCO_3$ increased the hardness property of banana filled greenpoxy composite insignificantly. However, a hybrid biocomposite with 3 wt.% of nano-$CaCO_3$ offered a superior hardness property.

Table 8.3: Impact and harness properties of unfilled, fiber-filled biocomposite, and nano-shell and plant fiber-filled hybrid biocomposite

.

Biocomposite	**Impact strength (KJ/m^2)**	**Hardness, H_b**
Neat greenpoxy (Control)	2.51± 0.03	23.8 ± 0.2
Greenpoxy + fiber	2.81 ± 0.02	32.3± 0.2
Greenpoxy + fiber + 1 wt.% nano-$CaCO_3$	2.9 ± 0.02	34.7 ± 0.1
Greenpoxy + fiber + 2 wt.% nano-$CaCO_3$	3.6 ± 0.01	33.25 ± 0.2
Greenpoxy + fiber + 3 wt.% nano-$CaCO_3$	2.9 ± 0.03	35.05 ± 0.2
Greenpoxy + fiber + 4 wt.% nano-$CaCO_3$	3.4± 0.02	34.7 ± 0.2
Greenpoxy + fiber + 5 wt.% nano-$CaCO_3$	2.9 ± 0.002	35.1 ± 0.1

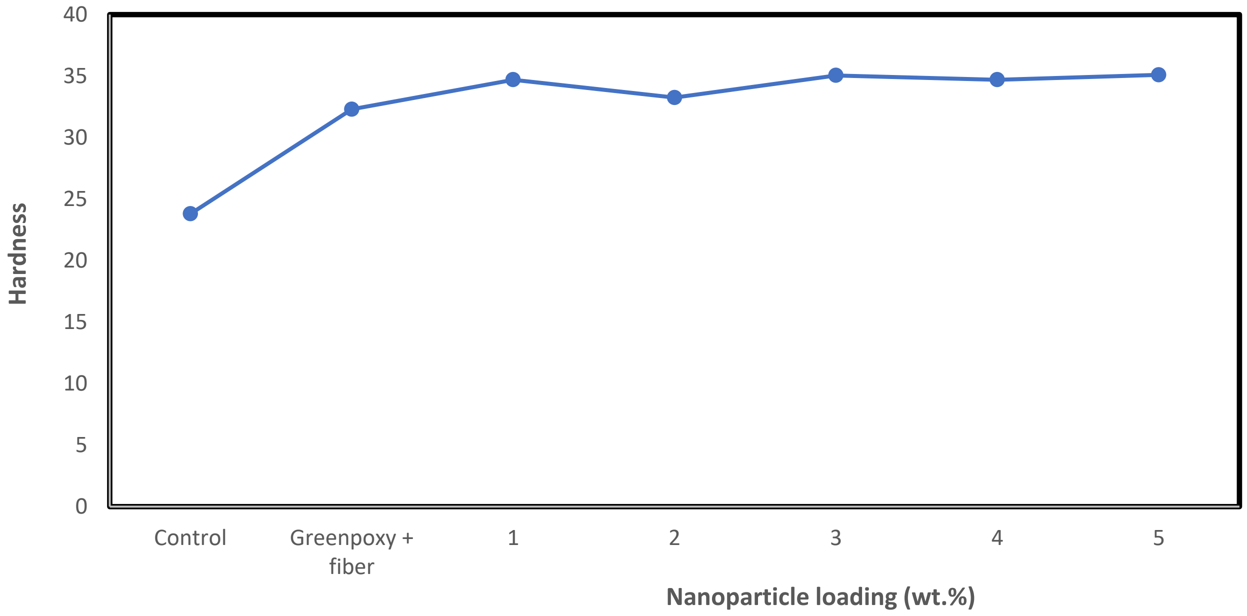


Figure 20: Graph showing hardness property of unfilled greenpoxy, banana filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite.

A slight increase in the hardness in proportion to the inclusion of nano-$CaCO_3$ may be due to the nanoparticles incorporated with a high hardness index. This trend is consistent with reports where it was observed that fillers' inclusion enhances the hardness property of biocomposite [42, 137, 255].

8.5.5 Impact strength

Figure 8.7 presents the impact strength of unfilled greenpoxy and banana filled greenpoxy composite and hybrid nano-shell plant fiber biocomposite. It was observed that the loading of banana fiber increased greenpoxy shock resistance by 11%. This increase in strength may be attributed to solid adhesion at the fiber and matrix interface. Further improvement in the energy absorption property of hybrid nano-shell plant fiber biocomposite was increase with nano-$CaCO_3$ loading.

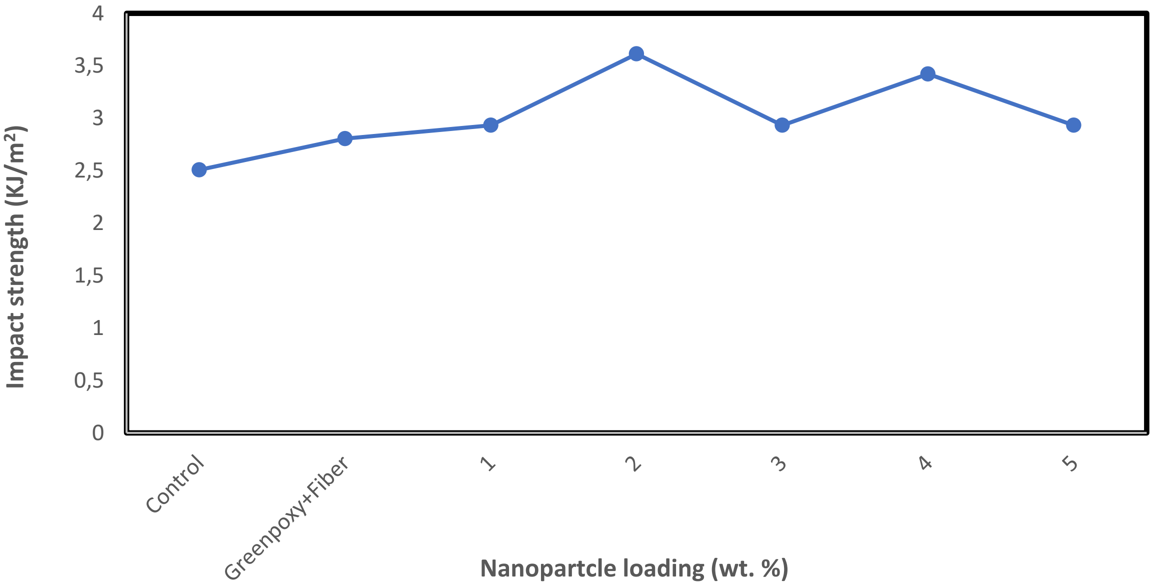


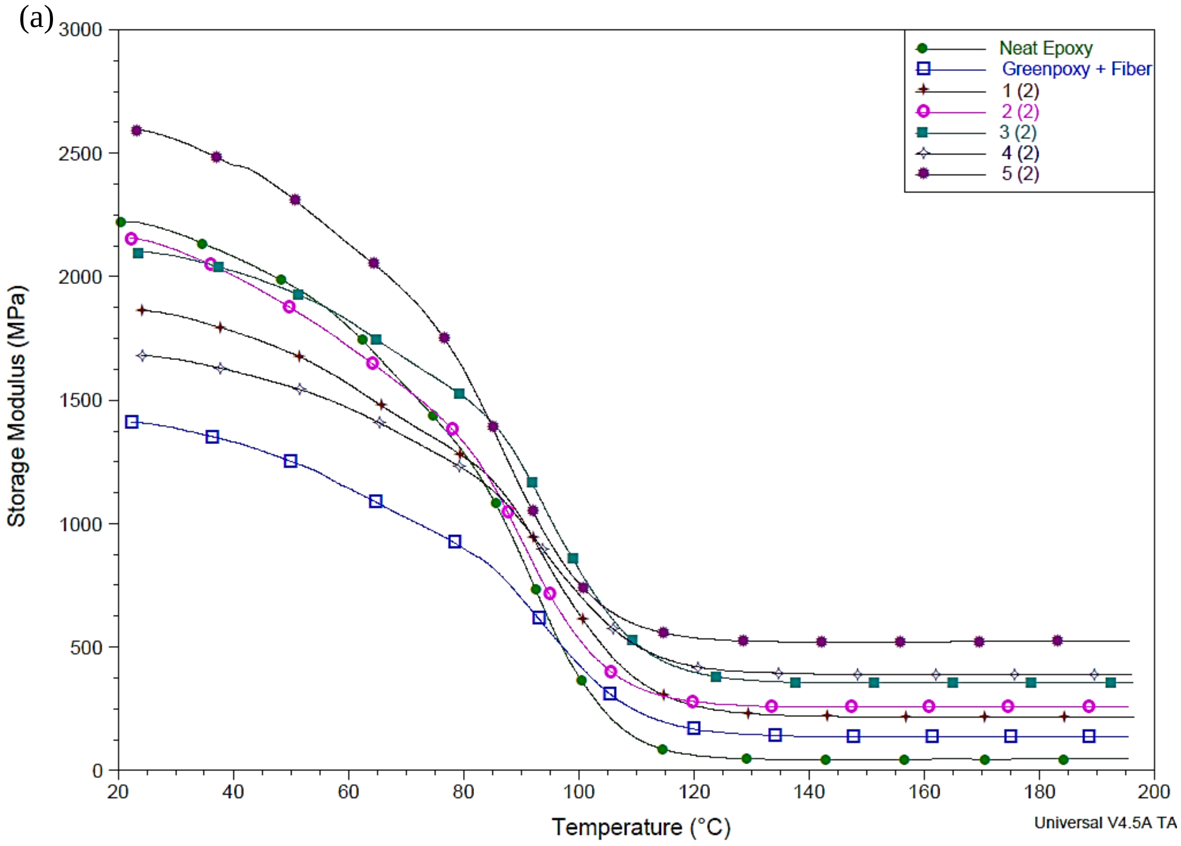
Figure 21: Graph showing impact strength of unfilled greenpoxy, banana filled greenpoxy biocomposite and hybrid nano-shell plant fiber biocomposite

Although an increase in shock resistance property banana filled greenpoxy composite irrespective of volume ratio incorporated, banana-filled greenpoxy biocomposite with 2 wt.% nano-$CaCO_3$ offered higher impact strength. Many similar reports of improved impact properties with the loading of nano-$CaCO_3$ were obtained elsewhere [256-258]. Notably, the loading of nano-$CaCO_3$ ranges from 1 wt.% to 2 wt.% increased impact strength of banana filled greenpoxy biocomposite by 4.34%, 29%, 4.3%, 22%, and 4,3%, respectively. The improvement in the energy-absorption property of hybrid biocomposite may be attributed to homogeneous dispersion and synergistic interlocking structure formed by the reinforcement and matrix. The presence of protein fibers in the *Achatina Fulica* shell particles may also be attributed to improved impact property [42, 259].

8.5.6 Dynamic Mechanical Analysis (DMA)

DMA's result on the rectangular specimens cut from pure greenpoxy and the developed biocomposite using dynamic mechanical analysis in tensile mode is reported in Figure 8.8. The distinction of temperature dependence storage modulus (E'), loss modulus (E"), and tan δ of samples from unfilled greenpoxy, banana filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite is as reported in Figures 8.8 a-c. A decrease in storage modulus with a corresponding increase in temperature was observed. Figure 8a shows that the loading of banana fiber drastically reduced the E' of neat greenpoxy at the glassy region and increasing E' values at the rubbery plateau. This decrease in E' values at the glassy region may be due to the dilution of the polymer and degree of freedom at the atomic level because free molecular mobility of the polymer chains often breaks the cross-linking existing between the molecular chains.

Furthermore, an increase in E' was observed for composite filled with fiber only in the rubbery region. This performance indicates the effectiveness of loading 20% banana fiber in the composite. This outcome, consistent with the result reported elsewhere [92, 260].



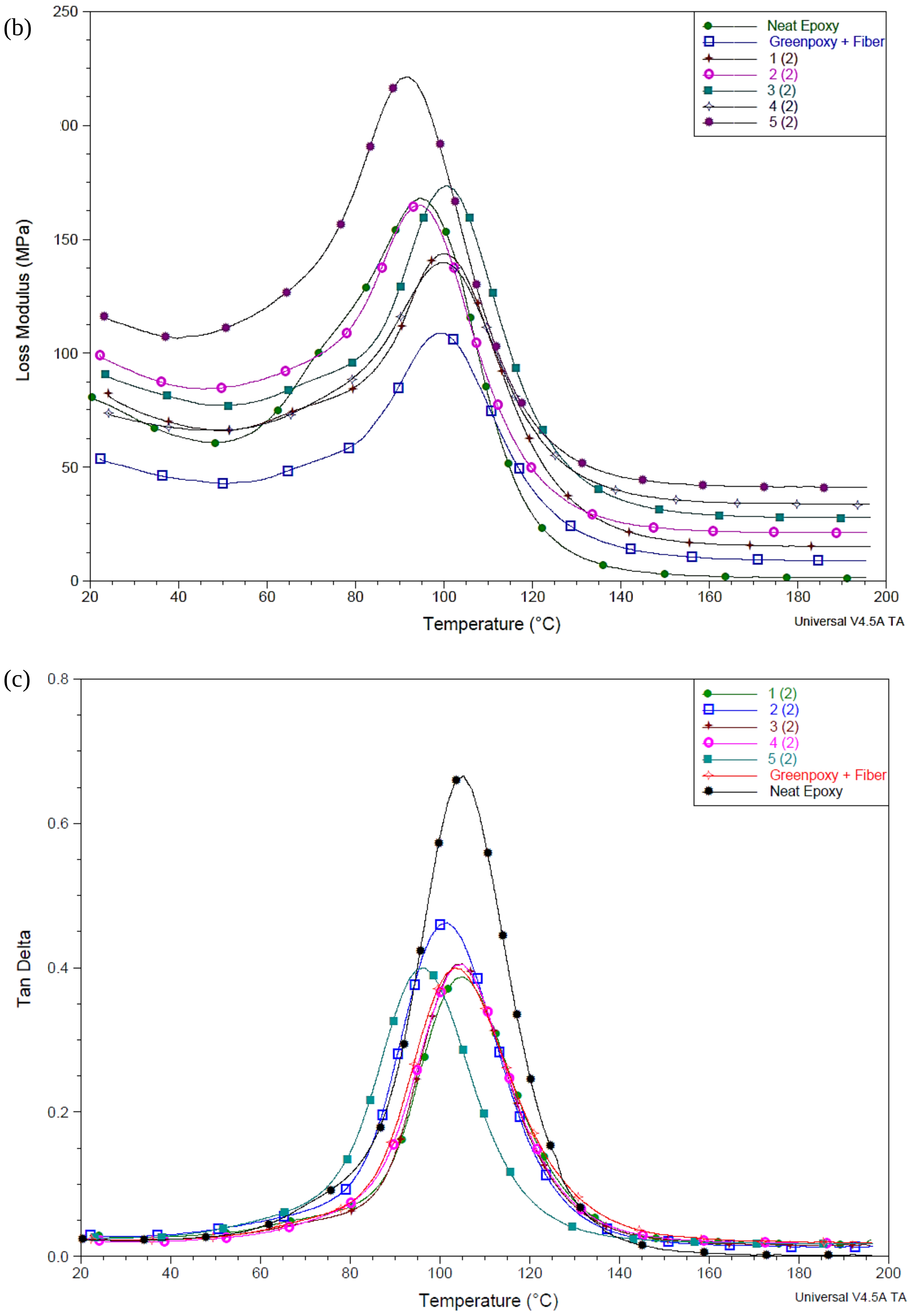


Figure 22: Temperature dependence; (a) storage modulus (b) loss modulus (c) Tan δ of unfilled greenpoxy, banana filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite.

It was observed that the loading of nano-$CaCO_3$ enhanced the storage modulus of greenpoxy/banana fiber biocomposite is proportional to a corresponding increase in nano-$CaCO_3$ concentration. This increase in E' of this biocomposite series may be due to the reduction in polymeric chain movement because nanoparticles are stiffer than greenpoxy and banana fiber, eventually modifying hybrid biocomposites and improving E' [261, 262]. A 43% increase in RT storage was obtained after loading 5% wt nano-$CaCO_3$ than greenpoxy and other biocomposite series. The performance may be attributed to the sophisticated interfacial adhesion, stiffness, and excellent thermal properties of nanoparticle and protein molecules in the nano-$CaCO_{3,}$ which modifies greenpoxy/banana fiber biocomposite, resulting in improved performance modulus. It may also be attributed to the synergistic effect form by the nanofiller, banana fiber, and greenpoxy matrix that produced a formidable structure that enhanced the stress transfer rate from the matrix to the reinforcement [262, 263].

Figure 8.8b shows that the loading of banana fiber decreases greenpoxy dissipating heat energy due to limited viscous motions within the fiber and matrix. The decrease in the dissipation of the heat energy capacity of the banana fiber-filled composite may be a result of the softness of the matrix when exposed to heat. An increase in the melt viscosity of banana fiber-filled greenpoxy biocomposite was observed after incorporating nano-$CaCO_3$ with excellent thermal properties, heat absorption, and dissipation. A significant increase in intensity E" at lower processing temperature was recorded at 5 wt% nano-$CaCO_3$ incorporations. This thermal incident indicates an increased melt viscosity of the biocomposite, which can be attributed to the high loading of nano-$CaCO_{3,}$ which helps the heat energy dissipation due to viscous motions within the mixture. Loading of 5 wt% nano-$CaCO_3$ thickens the blend and reduces viscous motion by replacing polymer-polymer hydrogen bonding with plasticizer hydrogen bonding [264].

A decrease in the peak intensity of loss modulus was observed for biocomposite without nano-$CaCO_3$ and biocomposite with only banana fiber having the lowest peak. The fall in the E" of biocomposite with only banana fiber recommends reducing melt viscosity due to weak interface bonding and heat energy dissipation of the natural fiber incorporated. Besides, the bonding process enhances the workability and processability of neat epoxy, eventually reduced its viscosity at the processing temperature. The loading nano-$CaCO_3$ of below 5 wt% into banana fiber-filled greenpoxy composite shifts the processing temperature and E" of the hybrid biocomposite. A significant increase in the E" and processing temperature of the hybrid composite was actualized at 3 wt% nano-$CaCO_3$ loadings. A shift in processing temperature better than 5 wt% loadings was observed at lower loading of 3 wt%. This outcome may be attributed to the grain's homogeneous dispersion and the effectiveness of low concentration loading. This performance depicts that the low incorporation of nano-$CaCO_3$ may significantly increase the viscosity of hybrid biocomposite compositions by acting as excellent plasticizers [35, 36].

The damping factor (Tan δ) examined for all the samples is as illustrated in Figure 8.8c. The Tan δ of unfilled greenpoxy is greater than all banana-filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite samples at glassy plateau may be due to more freedom in the atomic levels within the polymer structure [260]. It was observed that the damping factor of greenpoxy was reduced after banana fiber loading. This reduction may be attributed to a deficiency in fiber heat dissipation. An insignificant shift in the damping factor was observed for banana fiber-filled biocomposite with the loading of nano-$CaCO_3$. It was observed that hybrid biocomposite with 2 wt% nano-$CaCO_3$ exhibited a slightly higher tan δ peak (≈0.462) than other biocomposites. Hybrid biocomposite with 1 wt%, 3wt%, 4 wt% and 5 wt% showed tan δ peaks of 0.388, 0.405, 0.386 and 0.399.

The slight higher in damping factor at a lesser degree exhibited by 2 wt% nano-$CaCO_3$ indicates insufficient adhesion within the blend, resulting in high dissipation of energy than other biocomposites. Biocomposite with 1 wt% and 3wt% nano-$CaCO_3$ showed that strain is applied to blend to an advanced temperature, which eventually led to a more dissipative constituent of the blend. It was also observed that the width damping factor of neat greenpoxy becomes narrow with banana fiber and nano-$CaCO_3$ incorporation. This thermal incident depicts that the loading of banana fiber and nano-$CaCO_3$ helps relax the original molecular content of pure greenpoxy.

8.5.7 Water Uptake

The water uptake (WU) for pure green poxy, banana fiber-filled greenpoxy and biocomposite banana fiber-filled greenpoxy hybrid biocomposite series is shown in Figure 8.9. It was observed that the addition of banana fiber significantly increased the absorption rate of banana fiber-filled greenpoxy. The hydrophilic nature of the naturally sourced fiber allows water permeation into the fiber, extended to nanoparticle and matrix interface region, increased water sensitivity of the biocomposite leading to higher WU [265]. The hollow features of the fiber and change in the original molecular structure after banana fiber incorporation may be another reason for WU's high rate. In contrast, the loading of nano-$CaCO_3$ up to 3 wt% drastically reduced WU, and a sharp increase was observed afterward.

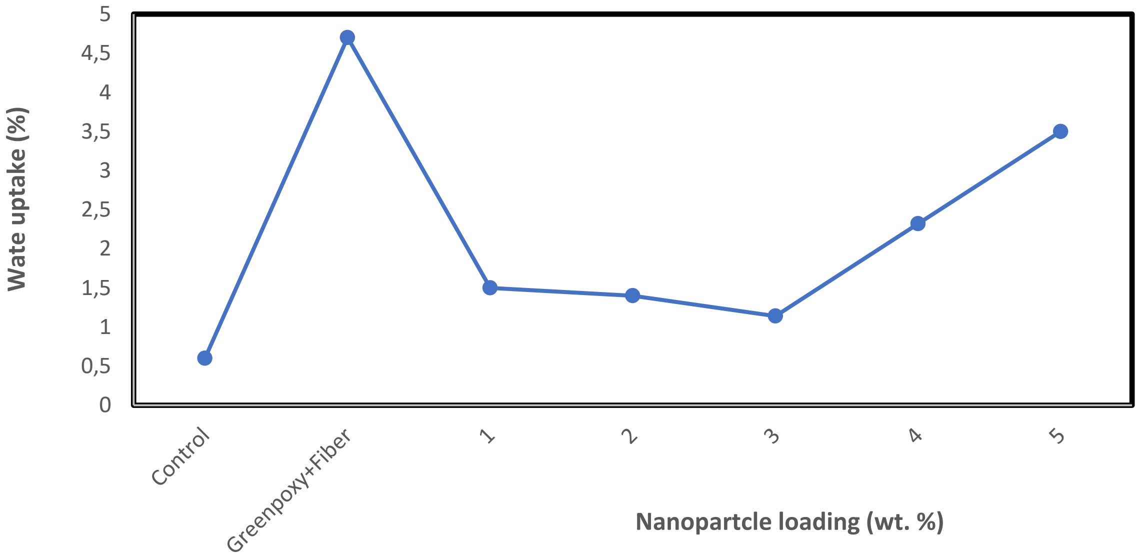


Figure 23: Water uptakes of unfilled greenpoxy, banana filled greenpoxy composite, and hybrid nano-shell plant fiber biocomposite.

A decrease in WU from 4.7% to 1.5% to 1.4% to 1.14% was observed, with an increase in nano-$CaCO_3$ loading up to 3 wt%. The decrease in the water absorption rate may have attributed to closer packing and homogenous dispersion of the nano-$CaCO_3$, producing a more substantial structure that resists water penetration. This trend is consistent with literature where loading of nano-$CaCO_3$ synthesized from shell reduced water uptakes [42, 193].

Furthermore, a significant decrease in WU of hybrid biocomposite can be directly ascribed to the hydrophobic nature of the nano-$CaCO_3$ and the interrelating bonds formed at the interface of filler, fiber, and matrix. The chemical treatment given to fiber and nano-$CaCO_3$ may be another reason for the reduction in WU. Another reason for the lesser water absorption rate of hybrid biocomposite may be due to the hydrophobic nature of the nano-$CaCO_{3.}$ A slight increase in WU was observed for hybrid biocomposite with 4 wt%. And 5 wt% loading of nano-$CaCO_{3.}$ This slight increase in WU can be attributed to the relative increase in the loading of nano-$CaCO_{3,}$ forming a particle agglomeration structure with weak resistance to water intake.

8.5.8 SUMMARY

A novel hybrid nano-calcium carbonate ($CaCO_3$) and banana fiber-reinforced biocomposite were successfully developed and investigated. The loading of Banana fiber of the exact length sizes (30mm) was kept constant (20%), and various loading of nano-calcium carbonate ($CaCO_3$) (1-5 wt%) synthesized from *Achatina Fulica* snail shell was combined with greenpoxy to fabricate hybrid biocomposite using hand lay-up method. The mechanical, microstructure, dynamic mechanical, and water uptake properties of the hybrid biocomposite were investigated and compared. The results show that the loading of banana fiber increased the mechanical properties of neat greenpoxy and negatively affected thermal properties and water uptake of the banana filled greenpoxy biocomposite. Improvement in strength was attributed to reinforcement properties and the load-carrying capacity of the fiber. However, the poor thermal properties and hydrophilic nature of the fiber harm DMA and water uptake. The loading of nano-calcium carbonate ($CaCO_3$) up to 2wt.% into banana filled greenpoxy biocomposite further increased the mechanical properties and higher loading of nano-calcium carbonate ($CaCO_3$) above 2wt%, decrease the properties. The DMA results are evidence that the loading of the banana fiber reduces the damping factor greenpoxy. It also indicates that the addition of nano-calcium carbonate ($CaCO_3$) increases the damping factor of banana filled greenpoxy biocomposite. The banana fiber loading reduces the storage modulus at the glassy phase; however, an increase in the rubbery phase's storage modulus was observed. The loading of nano-calcium carbonate ($CaCO_3$) affects the storage modulus of banana filled greenpoxy biocomposite in a glassy phase and rubbery phase. The rubbery phase storage modulus of hybrid biocomposite increased than unfilled greenpoxy and banana fiber-filled composite.

On the contrary, an adverse effect was observed at the glassy phase of hybrid biocomposite, except for hybrid biocomposite with 5 wt.% nano-calcium carbonate ($CaCO_3$) that exhibited higher storage modulus in the glassy phase. An increase in water uptake was observed after adding banana fiber into greenpoxy, and a drastic reduction was observed with the addition of nano-calcium carbonate ($CaCO_3$). The chemical treatment given to fiber and nano-$CaCO_{3,}$ the hydrophobic nature of the nano-$CaCO_{3,}$ was attributed to a reduction in water-up of hybrid composite. Improved thermal, mechanical properties of hybrid biocomposite suggest material for automobile interior panels

8.6 RESEARCH OUTPUT

Gbadeyan O.J, Adali S., Bright G., and Sithole B., "Mechanical, dynamic mechanical and thermal properties of hybrid nano-shell plant fiber biocomposite." *Submitted to Journal of Composite Material. Revised (under-review). (Manuscript number* JCM-20-1419*)*

CHAPTER NINE: CONCLUSIONS AND RECOMMENDATIONS

9.1 SUMMARY

The conclusion of the research work presented for the doctoral thesis are summarised as follows:

A novel calcium carbonate particle was produced from the *Achatina Fulica* snail shell. The chemical composition and thermal of the shell were characterized to determine thermal stability, degradation properties and identify the functional groups, elemental composition, carbonate ion, and mineral present in the shell. A high carbon, oxygen, and calcium level was the shell's main elemental composition; that is, the shell contains 99.4% of calcium carbonate ($CaCO_3$), with a high carbonate concentration of ions (CO_3^{2-}). The high concentration of calcium carbonate shells offered excellent thermal stability, suggesting that Achatina Fulica shell may produce low-cost biofillers and calcium carbonate ($CaCO_3$), which may be an alternative to expensive commercial fillers.

The snail shell was further investigated for micro-hardness and morphological properties for beneficiation into biocomposites. The outer prismatic layer of the shell exhibited higher resistance to indentation loading than the inner layer; good hardness values with high correlation coefficients were determined. SEM images of the nacreous layer exhibited an aragonite platelet layer structure that presumably serves as reinforcement that supports the prismatic layer, which reduced plastic deformation of the shell resulting in relatively high resistance to indentation and plastic deformation. These results suggest that the snail shells could be used as a filler material (micro or nano-size) to reinforce polymer materials.

The process of obtaining calcium carbonate nanopowders of different sizes from *Achatina Fulica* shells includes two phases: dry and wet milling in a planetary ball mill through mechanochemical techniques. In the first phase, the collected shell was dry milled and mechanical sieving to ≤ 50 µm. Lesser particle sizes were difficult to achieve because of particle agglomeration in steel jars. In this regard, shell particles were wetly milled afterward with four different solvents (Water, Methanol, Ethylene glycol, Ethanol**)** and washed using the decantation method. A random nanoparticle size ranging from 11.56 - 180.06 nm of calcium carbonate was achieved after dry and wet milling processes, and the smallest organic particle size with the average size ranging within 13.48 - 42.90 nm was obtained nano-calcium carbonate synthesis with ethanol. The effect of solvent on the chemical characteristics such as functional group, elemental composition, and carbonate ion of calcium carbonate nanopowders obtained from the *Achatina Fulica* shell was investigated. This technique has shown that calcium carbonate nanoparticles can be produced at a low cost, with low agglomeration, uniformity of crystal morphology, and structure from the *Achatina Fulica* shell. It also proved that the solvents used for milling have no adverse effect on the chemical properties of the nano- $CaCO_3$ produced.

The mechanical properties such as tensile strength, Young's modulus, impact strength, hardness, and water absorption properties of epoxy composites reinforced by *Achatina Fulica snail* (S-shell) compared with eggshell particles (E-shell) of the exact micro sizes of ≤ 50 μm. It was observed that the addition of shell particles improves the mechanical properties of neat epoxy irrespective of the percentage weight of the reinforcement. The mechanical and water absorption properties of composites and hybrid composites varied depending on the reinforcement concentration, and composite reinforced with S-shell offer higher properties than (E-shell) particles reinforced composite. These improved properties were attributed to the high percentage weight of calcium carbonate in these naturally sourced fillers, and the synergistic effect of the S-shell and E-shells particle can be attributed to high strength, stiffness, and decrease in water uptake of the composites.

The reinforcement properties of novel nano-calcium carbonate synthesized from *Achatina Fulica* snail shells were investigated. Thermo-mechanical of nano-calcium carbonate reinforced nanocomposite was determined. It was found that the loading of *Achatina Fulica* snail shell nanoparticles improved the thermal stability and mechanical properties of neat epoxy, irrespective of percentage weight loading. It also improves tensile strength by 70%, stiffness by over 200%, impact strength by 25%, and hardness by 35%. The improved properties were attributed to the incorporated nanoparticle's inherent thermal properties, homogeneous dispersion, and loading of nanoparticles at a lower concentration.

Finally, a novel combination of nano-shell and plant fiber hybrid biocomposite was developed and investigated to achieve the last set of objects stated in chapter one. Nano-calcium carbonate ($CaCO_3$) ranging from 1 to 5 wt.% and 20 wt. % banana fiber-filled hybrid biocomposite were prepared using a hand lay-up. The mechanical, microstructure, dynamic mechanical, and water uptake properties of the hybrid biocomposite were investigated and compared. The results show that the loading of banana fiber increased the mechanical properties of neat greenpoxy and negatively affected thermal properties and water uptake of the banana filled greenpoxy biocomposite. Improvement in strength was attributed to reinforcement properties and the load-carrying capacity of the fiber.

On the other hand, the fiber's poor thermal properties and hydrophilic nature harmed DMA and water uptake. The loading of nano-calcium carbonate ($CaCO_3$) up to 2wt.% into banana filled greenpoxy biocomposite further increased the mechanical properties and higher loading of nano-calcium carbonate ($CaCO_3$) above 2wt.%, decrease the properties. The DMA results are evidence that the loading of the banana fiber reduces the damping factor of greenpoxy. It also indicates that the addition of nano-calcium carbonate ($CaCO_3$) increases the damping factor of banana filled greenpoxy biocomposite. The banana fiber loading reduces the storage modulus at the glassy phase; however, an increase in the rubbery phase's storage modulus was observed. The loading of nano-calcium carbonate ($CaCO_3$) affects the storage modulus of banana filled greenpoxy biocomposite in a glassy phase and rubbery phase. The rubbery phase storage modulus of hybrid biocomposite increased than unfilled greenpoxy and banana fiber-filled composite.

On the contrary, an adverse effect was observed at the glassy phase of hybrid biocomposite, except for hybrid biocomposite with 5 wt.% nano-calcium carbonate ($CaCO_3$) that exhibited higher storage modulus in the glassy phase. An increase in water uptake was observed after adding banana fiber into greenpoxy, and a drastic reduction was observed with the addition of nano-calcium carbonate ($CaCO_3$). The chemical treatment given to fiber and nano-$CaCO_{3,}$ the hydrophobic nature of the nano-$CaCO_{3,}$ was attributed to a reduction in water-up of hybrid composite. Improved thermal, mechanical properties of hybrid biocomposite suggest material for the interior panels of the automobile, railways, and marine vehicles

9.2 Recommendations

Completing this research brought forth certain boundaries and, consequently, provides opportunities for more research work. Predictably, addressing these fundamental limitations may help future researchers realize the goal of producing more bio-based nanoparticles from naturally sourced material and producing biobased hybrid biocomposite to be used as interior part or functional components railways, marine, and automobile vehicles. The following section detailed the recommendations for future research.

9.2.1 Exploring more snail shells

This study confirmed that are many snail shells discarded and regarded as waste. Exploring through biorefining of these shells to usage material will reduce environmental pollution and add economic values to the shell, which benefits the economy and creates jobs.

9.2.2 Replications of snail shell structure for biocomposite development

This research studied *Achatina Fulica* shell morphology to determine the reinforcement suitability and fundamental properties of the shell. Imitating *Achatina Fulica* shell morphology for design synthetic processes to fabricate new bioinspired composites or biocomposite with required properties needs to be explored.

9.2.3 Milling processes

One of the drawbacks of this study included but was not limited to the long milling period of the shells. Thus, reducing the milling processing time for synthesizing nano-$CaCO_3$ from *Achatina Fulica* shell shall be a potential area for future work.

9.2.4 Fiber length and loading amounts.

In this research, 20% of banana fiber (30mm) was incorporated to produce biocomposite and recommend that different fiber lengths and loading could be explored. Reducing the length of fiber length further should allow higher loading of fiber in biobased polymer, enhance the homogeneity of fiber-matrix blends with improved mechanical properties and also provide a good understanding of the optimization of loading at smaller fiber sizes

9.2.5 Biodegradability

Since the biodegradability of biocomposite is not in the focuses of this present study, it recommended that studies for predicting the disintegration of biocomposite into CO2, H2O, and biomass should be done in the future. An investigation into Life cycle analysis and end-life recyclability of biocomposite will be possible to explore for future work.

CHAPTER TEN: REFERENCES

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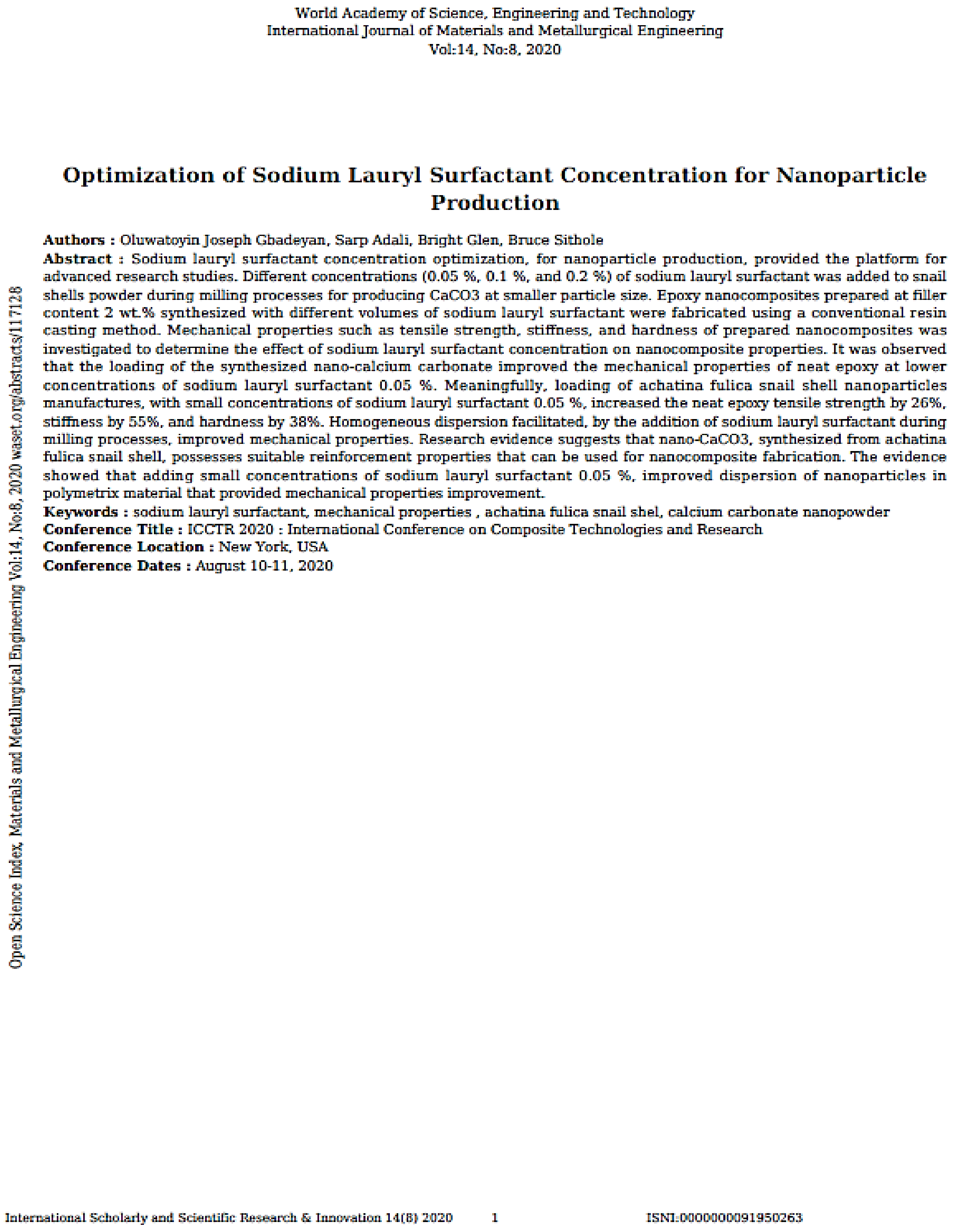
APPENDICES: Optimization of sodium lauryl surfactant concentration for nanoparticle production," Abstract accepted In The 22nd International Conference on Composite Technologies and Research, New York, USA during Aug 10-11, 2020 *(Published version)*



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Optimization of Sodium Lauryl Surfactant Concentration for Nanoparticle Production

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Abstract : Sodium lauryl surfactant concentration optimization, for nanoparticle production, provided the platform for advanced research studies. Different concentrations (0.05 %, 0.1 %, and 0.2 %) of sodium lauryl surfactant was added to snail shells powder during milling processes for producing CaCO3 at smaller particle size. Epoxy nanocomposites prepared at filler content 2 wt.% synthesized with different volumes of sodium lauryl surfactant were fabricated using a conventional resin casting method. Mechanical properties such as tensile strength, stiffness, and hardness of prepared nanocomposites was investigated to determine the effect of sodium lauryl surfactant concentration on nanocomposite properties. It was observed that the loading of the synthesized nano-calcium carbonate improved the mechanical properties of neat epoxy at lower concentrations of sodium lauryl surfactant 0.05 %. Meaningfully, loading of achatina fulica snail shell nanoparticles manufactures, with small concentrations of sodium lauryl surfactant 0.05 %, increased the neat epoxy tensile strength by 26%, stiffness by 55%, and hardness by 38%. Homogeneous dispersion facilitated, by the addition of sodium lauryl surfactant during milling processes, improved mechanical properties. Research evidence suggests that nano-CaCO3, synthesized from achatina fulica snail shell, possesses suitable reinforcement properties that can be used for nanocomposite fabrication. The evidence showed that adding small concentrations of sodium lauryl surfactant 0.05 %, improved dispersion of nanoparticles in polymetrix material that provided mechanical properties improvement.

Keywords : sodium lauryl surfactant, mechanical properties , achatina fulica snail shel, calcium carbonate nanopowder
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