EFFECTS OF CALCINED BALL CLAY FILLER ON MECHANICAL PROPERTIESOF HIGH-DENSITY POLYETHYLENE COMPOSITE USED FOR MAKING AUTOMOBILE PARTS

BY

ONUORAH, Emmanuel Somuadina

MEng/SEET/2017/7258

DEPARTMENT OF CHEMICAL ENGINEERING

FEDERAL UNIVERSITY OF TECHNOLOGYMINNA

OCTOBER, 2022

EFFECTS OF CALCINED BALL CLAY FILLER ON MECHANICAL PROPERTIESOF HIGH-DENSITY POLYETHYLENE COMPOSITE USED FOR MAKING AUTOMOBLE PARTS

BY

ONUORAH, Emmanuel Somuadina
MEng/SEET/2017/7258

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY MINNA, NIGERIA IN PARTIAL

FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREEOF MASTER OF ENGINEERING IN CHEMICAL ENGINEERING

OCTOBER, 2022

ABSTRACT

The thesis describes the preparation of the composite materials of high density polyethylene (HDPE) and raw ball clay, HDPE and ball clay calcined at 700◦C under the same percentage weight variation using injection moulding machine operated at a temperature of 160◦C. Some mechanical properties vital in automobile parts- impact strength and tensile strength at yield were determined at different weight fraction of filler (0%, 5%, 10%, 15%, 20% 25%, 30%) in accordance with ASTM D256 and ASTM D638 method respectively. The virgin HDPE used was sourced from Indorama Eleme petrochemical Ltd along with the technical data sheet containing its mechanical properties. The X-ray diffraction (XRD) analysis was carried out to investigate the phase composition, crystalline structure and the degree of disorderliness of raw ball clay and calcined ball clay. The Raw ball clay and calcined ball clay were subjected to scanning electron microscope (SEM) to obtain more understanding on the structures and size distributions of the samples. The results for Thermogravimetric analysis (TGA) curves for pure HDPE, HDPE-calcined ball clay (CBC) composite and HDPE-raw ball clay (RBC) composite for the temperature range 0-600°C shows some weight losses. It was deduced that weight loss in sample 100HDPE begins at 360°C while for 95%HDPE/5%CBC, 85%HDPE/15%CBC and 70%HDPE/30%CBC weight lose starts at 430°C. This indicate that calcination of ball clay improves the TGA of the matrix material. Weight loss for various weight fraction of HDPE-RBC begin around 150°C. This show that calcination of ball clay improves the TGA of HDPE-Ball clay composite. Results showed that there was an improvement on the mechanical properties as the filler content increases. Calcined ball clay produces better mechanical properties than raw ball clay. As the filler loadings were increased to a significant amount, the mechanical properties started to reduce. Reinforcing High Density Polyethylene (HDPE) with Raw and Calcined ball clay significantly improves the Tensile strength at yield, and Impact strength of HDPE. Calcined Ball clay-HDPE composite produces better mechanical properties than raw ball clay-HDPE composite. 75% HDPE/25%CBC and 70%HDPE/30%CBC produces has the highest impact and tensile strength of 119.5 J/m and 68.9 Mpa respectively and can be used in the manufacture of automobile parts like car bumper.

TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Materials are probably more deep-seated in our culture than most of us realized. Housing, transportation, clothing, communication, recreation, and food production-virtually every segment of our everyday life is influenced to one degree or another by materials. Historically, the development and advancement of societies have been intimately tied to the members' ability to produce and manipulate materials to fill their needs. In fact, early civilizations have been designated by the level of their materials development (Stone Age, Bronze Age, and Iron Age), (William *et al.*, 2007). Solid materials have been easily arranged into three main categories: metals, ceramics, and polymers. This classification is established primarily on chemical makeup and atomic structure, and most materials fall into one particular grouping or another, although there are some in-betweens.

Ceramics are compounds between metallic and non-metallic elements; they are most commonly oxides, nitrides, and carbides. For example, some of the common ceramic materials include aluminium oxide (or alumina, Al_2O_3), silicon dioxide (or silica, SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), and, in addition, what some refer to as the traditional ceramics those composed of clay minerals (i.e., porcelain), as well as cement and glass. With regard to mechanical behaviour, ceramic materials are relatively stiff and strong stiffness and strengths are comparable to those of the metals. In addition, ceramics are typically very hard. On the other hand, they are highly brittle (lack ductility) and are highly susceptible (William *et al.*, 2007). Ceramic is a clay material that is shaped into the desired forms and then fired to produce desired properties. Ball clay is vital ingredient in ceramic manufacturing. Most of the ceramic products such as pottery, stoneware, sanitary ware and dinnerware consist of ball clay in their formulation (Baioumy *et al*., 2014). Ball clays are kaolinitic sedimentary clays that commonly consist of 20–80% kaolinite, 10–25% mica, 6–65% quartz. Localized seams in the same deposit have variations in composition, including the quantity of the major minerals, accessory minerals and carbonaceous materials such as lignite. According to British Geological Survey (2011), ball clays are fine-grained, high plastic sedimentary clay, when fired will produce a light or near white colour (Grim *et al.*, 1968). Nigeria has high quality ball clay deposits at Niger, Abia, Ogun, Kaduna, Kano, Kogi, Enugu, Benue and River States (http://www.nigeria.gov.ng).

Composite material is the assembly of two or more materials, the final assembly having properties superior to the properties of each of the constituent materials (Werken *et al*., 2020). In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics, and polymers to make a new generation of extraordinary materials. The nature of the matrix and the charge, the shape and proportion of charge, the quality of the interface and the production process used are all parameters that can influence the properties of the composite material (Khalil *et al*., 2011). Most composites have been created to upgrade combinations of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength (William *et al*., 2007). The design goal of a composite is to bring about a combination of properties that is not displayed by any single material, and also to combine the most excellent trait of each of the component materials. An enormous number of composite types exist that are represented by different combinations of metals, ceramics, and polymers. Composites provide rare combination of mechanical and physical properties that cannot be found in any single material. The insertion of reinforcements of good tensile strength, of very high modules in a polymer matrix, makes it possible to improve the mechanical and thermal qualities (Datsyuk *et al*., 2020). They are light in weight, hard, ductile, high temperature resistant as well as shock-resistant materials. Many composite materials are composed of just two phases; one is termed matrix phase, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. “Dispersed phase geometry” in this context means the shape of the particles and the particle size, distribution, and orientation (William *et al*., 2007).

Polyethylene is described as a semi-crystalline polymer, made up of crystalline regions and amorphous regions. Crystalline regions are those of immensely ordered, neatly folded, layered (in parallel) and densely packed molecular chains. These occur only when chains branching off the sides of the basic chains are small in number. Within crystalline regions, molecules have properties that are locally (within each crystal) directionally dependent. Where tangled molecular chains branching off the molecular trunk chains interfere with or inhibit the close and layered packing of the trunks, the random resulting arrangement is of lesser density, and called amorphous. A great amount of closely packed polymer chains results in a tough material of moderate stiffness. Polyethylene or polythene (PE), International Union of pure and Applied Chemist (IUPAC) name polyethene or poly(methylene), is the most common plastic. As of 2017, over 100 million tons of PE resins are produced annually, accounting for 34% of the total plastics market (Geyer *et al*, 2017).

High-Density Polyethylene (HDPE) resin has a relative amount of crystalline regions than Low-Density Polyethylene (LDPE). The size and size distribution of crystalline regions are determinants of the tensile strength and environmental stress crack resistance of the end product. HDPE, with fewer branches than Medium-Density Polyethylene (MDPE) or LDPE, has a greater proportion of crystals, which results in greater density and greater strength. Theoretically, an entirely crystalline polyethylene would be too brittle to be useful and an entirely amorphous polyethylene would be wax like, much like paraffin. Upon heating, the ordered crystalline structure reverts to the disorganised amorphous state; with cooling, the partly crystalline structure is recovered. The melting point of polyethylene is that temperature at which the plastic transitions to an entirely amorphous state. In HDPE and other thermoplastic materials, the molecular chains are not cross-linked and such plastics will dissolve with the application of a sufficient amount of heat. With the application of heat, thermoplastic resins may be shaped, formed, moulded or extruded. Therefore, addition of clay (raw or calcined) may improve some properties and make the composite suitable for some application as shown by Amit (2015).

1.1 Aim and Objectives

The aim of this research project is to determine the effect of raw and calcined ball clay filler on mechanical properties of high-density polyethylene composite vital in the making of automobile parts The objectives of this research includes the following;

1. To determine the various characteristics and chemicals composition of the raw and calcined ball clay fillers that will be used in this research.
2. To determine the effects of various weight fractions of the fillers that will be used for this research.
3. To determine the thermal stability of the high-density polyethylene raw and calcined ball clay composite.
4. To determine the composite that gives the best impact strength, thermal stability and tensile strength for the purpose of manufacturing car bumpers.

1.2 Scope of the Study

This research is limited to the production of HDPE-RAW Ball clay composite, HDPE-Calcined Ball clay composite, Calcination of ball clay, characterization of the raw ball clay and calcined ball clay, testing for the thermal stability, tensile strength, and impact strength of the HDPE-RAW ball clay and HDPE-CALCINED ball clay composites.

1.1 Relevance of the Study

This work was motivated by the abundant availability of ball clay in Niger state and the high cost of High-density polyethylene based engineering materials in Nigeria. Synthetic fillers used in reinforcing High density polyethylene are becoming more expensive than High density polyethylene- the matrix material. Hence the need to source for cheap, natural, and abundant fillers.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Polymers

Polymers are macro molecules composed of one or more chemical units/ monomers that are repeated throughout a chain (William *et al.,* 2007). The rise of polymers in the beginning of the nineteenth century led to a new era of research with a new possibility of using the natural fillers in more various fields. At the same time interest in synthetic fibers, because of its greater dimensional and other properties grew in popularity and gradually substituted the natural fibers in diverse applications. Conversely, change in the raw material and production of synthetic composites required a large quantum of energy and quality of environment suffered because of the pollution formed during the production and recycling of these synthetic materials. This has once again drawn the attention towards natural fillers has resulted in a large number of changes to bring it at par and even superior to synthetic fillers. Because of such remarkable changes in the quality of natural fillers, they are fast emerging as a reinforcing material in composites. Considering the high performance standard of composite materials in terms of durability, maintenance and cost effectiveness, applications of natural fiber reinforced composites as construction material in creating built environment holds the huge prospect and are critical for attaining sustainability.

Depending on the how they are linked or joined and on the arrangement of the different chains that form the polymer, the resulting polymeric material can be classified as:

- Thermoplastics
- Elastomers
- Thermosets

On the basic of source, there are Natural polymers, which include starch, cellulose, protein, Nucleic acid, Natural rubber etc.

2.2 Polyethylene

Polyethylene is categorised as a semi-crystalline polymer, made up of crystalline regions and amorphous regions (William *et al.,* 2007). Crystalline regions are those of greatly ordered, neatly folded, layered (in parallel) and tightly packed molecular chains. These occur only when chains branching off the sides of the primary chains are small in number. Within crystalline regions, molecules have properties that are locally (within each crystal) directionally dependent. Where tangled molecular chains branching off the molecular trunk chains affect or inhibit the close and layered packing of the trunks, the random resulting arrangement is of lesser density, and termed amorphous. An abundance of thoroughly packed polymer chains results in a tough material of moderate stiffness. High-density polyethylene resin has a higher amount of crystalline regions than low-density polyethylene. The size and size distribution of crystalline regions determine the tensile strength and environmental stress crack resistance of the end product. HDPE, with fewer branches than MDPE or LDPE, has a greater proportion of crystals, which results in greater density and greater strength. LDPE has a structure with both long and short molecular branches. With a lesser amount of crystals than HDPE, it has greater flexibility but less strength. LLDPE structurally differs from LDPE in that the molecular trunk has shorter branches, which help to inhibit the polymer chains becoming too closely packed. Hypothetically, an entirely crystalline polyethylene would be too brittle to be useful and an entirely amorphous polyethylene would be wax like, much like paraffin. Upon application of heat, the ordered crystalline structure reverts to the disordered amorphous state; with cooling, the partially crystalline structure is recovered. This characteristic allows thermal welding of polyethylene to polyethylene.

The melting point of polyethylene is described as the temperature at which the plastic transitions to an entirely amorphous state. In HDPE and other thermoplastic materials, the molecular chains are not cross-linked and such plastics will melt with the application of adequate quantity of heat. With the application of heat, thermoplastic resins may be shaped, formed, moulded or extruded. Thermosetting resins are made up of chemically cross-linked molecular chains, which set at the time the plastic is first formed; these resins will not melt, but rather degenerate at a temperature lesser than its melting point, when enough heat is added.

During processing, elevated temperatures and energy associated with forming and shaping the polyethylene cause unsystematic alignments of molecules within the molten material to directionally align in the extruding orifice. At room temperatures, the ordered arrangement of the layered crystalline polyethylene molecules is retained. Tie molecules link the crystalline and amorphous regions. When the capacities of the polymer chains are overwhelmed by tension, the polymer flows (alters its shape). Tensile forces (stresses) then initiate brittle fracture, evidenced by cracking. In HDPE this may occur at very high strain rates. Once a crack is started, tensile forces (stresses), which were contained prior to the event of cracking, are released. These released tensile forces (stresses) are captured by the material at the leading tips of the crack, thereby significantly increasing the intensity of the stress field and the possibility of continued cracking at that point and all points forward.

The terms stress riser and stress intensity factor are used to classify and quantify the increase in the stress field at the tips of a crack. If these regions contain and adequately respond to this increased burden, then the cracks will not propagate; if they do not, crack propagation will result. This characterizes the mechanism of slow crack growth. Stress risers are proportional to the measure of stress. Cracks will not spread in a stress-free environment or where the level of stress at the tip of a crack is at a sufficiently low threshold. When the tip of a propagating crack leaves a crystal, it enters the disordered, non-layered, more loosely packed, tangled molecules of the amorphous region where the energy related with the stress field is partly dissipated as the tangled mass of molecules regulates in time to the sustained forces.

When polyethylene is pulled at low strain rates, in those areas where elongation has taken place, elongated rearrangement of the mass will be irreversible when molecular chains begin to slip by one another. Ultimate tensile strength occurs when the bonds between the molecular chains are fractured. The energy that would otherwise be stored in the system and which would otherwise be available to restore the region to its original geometry is dissipated and unrecoverable with the event of the fracture. The new arrangement of molecules alters the stress/strain response of the remaining region. With increasing load and fewer bonds to resist, the material is less stiff and therefore takes less force to cause a unit of deformation. This phenomenon is noted on a stress-strain curve by an ever-decreasing slope as the curve bends gradually to the right as the process continues. This is what describes strain softening, a characteristic of polyethylene and all materials that yield under increasing load. With sustained loads, the continuing distortion is known as plastic flow. If, at some point in the deformation process the deformation is maintained, the loads and resulting internal stresses relax. This process of change is called stress relaxation.

2.2.1 Physical properties of polyethylene

Polyethylene consists of a thermoplastic polymer consisting of long hydrocarbon chains (William *et al.,* 2007). Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium and high - density polyethylene, the melting point is typically in the range of 120 -180^{0}C .The melting point for average, commercial, low –density polyethylene is typically 105 -115^{0}C.

2.2.2 Chemical Properties of Polyethylene

Most polyethylene has an outstanding chemical resistance both for strong acid and bases, gentle oxidants and reducing agents. Polyethylene burns gradually with a blue flame having a yellow tip and gives off a paraffin odour. The material continues burning on the elimination of the flame source and produces a drip. They can be dissolved at elevated temperature in aromatic hydrocarbons such as toluene or xylene or in chlorinated solvents such as tri-chloroethane or tri-chlorobenzene.

2.2.3 Important properties of polyethylene

i. Extreme versatility and ability to be tailored to meet very specific technical needs.
ii. Lighter weight than competing materials reducing fuel consumption during transportation and processing.
iii. Extreme durability.
iv. Resistance to chemicals, water and impact.
v. Good safety and hygiene property for food packaging.
vi. Excellent thermal and electrical insulation properties.
vii. Relatively inexpensive.
viii. Have moderate high melting point.

2.2.4 Classification of polyethylene

Polyethylene is classified into various categories based frequently on it density and branching. Its mechanical properties depends significantly on variables such as the extent and type of branching ,the crystal structure and the molecular weight , with regards to their volumes, the most important polyethylene grades are HDPE, LLDPE and LDPE. There are also

i. Ultra – high – molecular weight polyethylene (UHMWPE)
ii. Ultra-molecular weight polyethylene (ULMWPE or PE WAX)
iii. High molecular weight polyethylene (HMWPE)
iv. High density polyethylene (HDPE)
v. High density cross –linked polyethylene (HDXLPE)
vi. Cross linked polyethylene (PEX o XLPE)
vii. Medium density polyethylene (MDPE)
viii. Linear low-density polyethylene (LLDPE)
ix. Low density polyethylene (LDPE)
x. Very low-density polyethylene (VLDPE)
xi. Chlorinated polyethylene (CEE)

2.2.5 High density polyethylene (HDPE)

2.2.5.1 Physical chemistry and mechanical properties of HDPE

High-density polyethylene (HDPE) (0.941 < density < 0.965) is a thermoplastic material composed of carbon and hydrogen atoms linked together forming high molecular weight products. Methane gas is converted into ethylene, then, with the application of heat and pressure, into polyethylene. The polymer chain may be 500,000 to 1,000,000 carbon units long. Short and/or long side chain molecules exist with the polymer’s long main chain molecules. The longer the main chain the greater the number of atoms, and consequently, the greater the molecular weight. The molecular weight, the molecular weight distribution and the amount of branching control many of the mechanical and chemical properties of the end product. The property characteristics of polyethylene hang on the arrangement of the molecular chains. The molecular chains, shown schematically in, are three-dimensional and lie in wavy planes. Not shown, but branching off the main chains, are side chains of varying lengths. The number, size and type of these side chains determine, in large part, the properties of density, stiffness, tensile strength, flexibility, hardness, brittleness, elongation, creep characteristics and melt viscosity that are the results of the manufacturing effort and can occur during service performance of polyethylene pipe. This is defined by a density greater or equal to 0.941, g/cm ^{3}, it has a low degree of branching and thus low intermolecular forces and tensile strength. HDPE can be produced by Chromium/Silica catalyst, Ziegler-Natta catalyst or metallocene catalysts. The lack of branching is ensured by a suitable choice of catalyst and reaction conditions. It is used in products and packaging such as milk jogs, detergent bottle, butter tubs, garbage containers such as milk jugs, detergent bottles, butter tubs garbage containers and water pipes. One third of all toys are manufactured from HDPE.

Table 2.1: Typical Properties of Some Polymer Matrix Materials at Room Temperature.

Material	Specific Gravity	Tensile Modulus (GPA)	Tensile Strength (MPA)	Yield Strength (MPA)	Elongation At Fracture (%)
Polyethylene (low density)	0.917-0.932	0.17-0.314	13.3 -24.2	9.0-14.5	100-160
Polyethylene (Highdensity)	0.952-0.965	1.06-1.09	22.1-31.0	26.2-3 3.1	100-200
Polypropylene (PP)	0.90-0.91	1.14-1.55	31.4-41.4	31.0-37.2	100-600
Polyester (PET)	1.29-1.40	2.8-4.1	48.3-72.4	59.3	30-300
Polycarbonate	1.2-1.32	2.38	62.8-72.4	62.1	110—150
Phenol formaldehyde	1.2-1.32	1.76-4.83	34.5-62.1	-	1.5-20
Nylon 6, 6	1.13-1.15	1.58-3.80	75.9-94.5	44.8-82.8	15-300

Source: Modern plastic Encyclopedia 96 (1995)

2.3 Benefits of using the polymer composites

Legislations for new vehicle designs are constantly getting stiffer in terms of environmental friendliness, fuel efficiency, recyclability, and safety of passengers and pedestrians. Change is therefore imminent in all areas of vehicle design in which material selection is core. Vehicle efficiency also increases through weight savings as about 40% of fuel consumption is attributed to inertia due to vehicle mass (Jeyanthi, 2013). The main benefits of polymer composites come from the result of combining the properties of the matrix materials. Fibrous materials are known to be very strong and stiff and polymers are generally lightweight and flexible materials. Thus, the composites combine both advantages including better physical properties, recyclability and cheaper cost in some cases.

Polymer matrix composites are produced such that mechanical loads are supported by reinforcement while the polymer matrix bonds the fibres together to share the loads between them. The mechanical properties of conventional materials for car bumpers and that of the polymer composites are compared using data collected from an encyclopaedia for engineering materials (CES EduPack 2015) shown in Table 2.2. In addition to their low densities, polymer composites also have other excellent physical properties. Polymer composites can be produced to have smooth surface finishes which is an important factor for aerodynamic drag. The car bumper is an exterior component of the vehicle and as such it has its own contribution to the total pressure drag the vehicle must overcome. Therefore, car bumpers made with polymer composites are beneficial in their contribution to weight reduction and drag reduction which cumulates to improved fuel consumption of a vehicle. In addition, polymer composites offer excellent resistance to corrosion and to chemical attack.

Table 2.2: Mechanical properties of materials for car bumper beam

	High strength steel	High strength al-alloy	Polypropylene Plastic	Carbon fibre-epoxy	Glass fibre Polypropylene	Nylon-6-nanoclay
Density (kg/m³)	7,800–7,900	2,500–2,900	890–910	1,400–1,700	1,320–1,340	1,130
Young's modulus (GPa)	200–221	68–80	0.90–1.55	69–150	10.40–11.70	5.00
Yield strength (MPa)	330–460	95–610	20.70–37.20	221–276	110–122	83.40–84.10
Tensile strength (MPa)	580–670	180–620	27.60–41.40	350–500	115–127	75.20
Elongation (% strain)	19–22.80	1–20	100–600	0.50–2.00	1.53–1.85	15
Shear modulus (GPa)	77.50–83.50	25–28	0.32–0.55	27.80–60.50	4.05–4.15	-
Fracture toughness (MPa √m)	43.40–62.50	21–35	3.00–4.50	25.8–38.3	5.11–5.37	4.03–4.50

SOURCE: encyclopedia for engineering materials (1990)

Description and Properties of a Car Bumper

Bumpers are essential parts of the crash management of a car. They are passive safety components that help to reduce aggressiveness of a crash. By placing them in the front end, they help to reduce physical damage and absorb shock at low impacts. In the earlier design of cars, bumpers were just rigid metal bars (IIHS, 2015). Later, thermoplastic elastomers were added as bumper covers (Drobny, 2014). Although the foam or honeycomb serves as the impact absorbing material and the plastic cover is useful for its aesthetics and protection purposes (Belingardi *et al.,* 2015), the beam is the major structural part and thus the component of interest. According to European Aluminium Association (2013), The car bumper has three major expectations, namely:

i. To minimise the damage of the vehicle at low and medium speed crashes

ii. To guide the crash forces into the body structure at high-speed crashes to reduce passenger component intrusion.

iii. To absorb energy at the start of a crash

As evident from the legislative expectation of a car bumper, the fundamental mechanical properties of the car bumper beam are strength and toughness. The strength of a beam is the magnitude of force it can withstand before deformation while toughness is its resistance to break or fracture under stress (Srinivasan, 2014). Another important property requirement is ductility, as the beam is expected withstand high level of deformation before fracture. The fracture of the car bumper after a collision could create a sharp end which itself constitutes a hazard. Although not as important as basic requirements, it is also desired that bumpers are built to last. To ensure this, the material selected must be able to withstand corrosion. Also, as it pertains to other vehicle components, there should be possibility and ease of large scale manufacturing for the materials used. For a component like the bumper beam which can remain intact throughout the lifecycle of the car, the material recyclability is also important if not necessary considering new and upcoming legislations, for instance the Project ICARRE 95 in Europe that requires 95% by average weight of all end-of-life vehicles to be reused or recovered (Miller *et al.*, 2014). Another important property which is also the motive of this research is that the car bumpers should also contribute to reduced weight and thus fuel efficiency of the vehicle.

2.5 Common materials for car bumper

2.5.1 Steel bumpers

Steel is the most common material used for automotive parts (Steel Market Development Institute, 2013). Steel beams have strength, stiffness and high energy absorption capacity making them very appropriate for car bumper. In addition to these key properties, they offer excellent resistance to corrosion, good fatigue properties and can be easily mass produced. These characteristics have made them well positioned in the bumper system market having 83% market share in 2013 (Steel Market Development Institute, 2013).

There are numerous steel grades available for manufacturers to choose from, ranging from mild steel to high strength steel and then ultra-high strength steel (UHSS). UHSS defined as steel with tensile strength above 700 MPa (Sutar *et al.,* 2015) is most commonly used for bumper beams (Steel Market Development Institute, 2013). Steel reinforcing beams are usually roll formed or hot stamped. Rolling is a method used in forming long cross-sections of steel from steel plates.

2.5.2 Aluminum bumpers

Aluminum is the second material of choice for vehicle parts and also common for bumper beams. Many manufacturers find it useful as it offers weight savings of up to 50% when compared with steel while still maintaining safety and performance in a cost-effective manner (Hirsch, 2011). In addition to the lower weight it offers, it meets the requirement of energy absorption and can also be mass produced (Hirsch, 2014).

2.5.3 Plastic bumpers

Plastic bumpers have been introduced in modern cars as they offer designers tremendous amount of freedom for styling. Plastics were once only used for fascia but currently, some vehicles use plastic reinforcing beams (American Chemistry Council, 2014). Some plastics commonly used today are polycarbonate/polybutylene, polyethylene and polypropylene (GV *et al.,* 2014). They have tensile strengths of up to 275 MPa and flexural moduli up to 15,000 MPa (Steel Market Development Institute, 2013).

The popular methods of fabricating plastic car bumper beams are injection moulding and compression moulding. By injection moulding, the polymeric powder is fed into a heated barrel and mixed, then forced into a mould cavity where it cools and hardens to the configuration of the cavity (James *et al.*,2006). For compression moulding, the polymeric powder is preheated and then placed in an open, heated mould cavity. The mould is then compressed at high pressure to force the material into contact with all mould areas (James *et al.,* 2006).

It is possible to use some polymer composites for bumper beams which are lighter than aluminum and also have the strength and stiffness required for crashworthiness. Plastics with about 30% reinforcement can yield composites with more than 100% increase in tensile strength and still offer lower weight and aesthetics (American Chemistry Council, 2014). There are various polymeric composites that have been formed and used in the material industry.

2.5.4 Carbon-fibre-epoxy composite

Epoxy resin is a thermosetting polymer with high adhesive strength and high mechanical properties and therefore used for applications such as electronics, adhesives, and structural composites (Wan *et al.,* 2014). When reinforced with carbon fibre, they form composites which exhibit special advantages over monolithic materials, such as high strength, high stiffness, long fatigue life, low density, corrosion resistance, wear resistance, and environmental stability (Tserpes *et al.*,2009).

Carbon fibre with epoxy offers a good balance for processing, part performance, and durability. Although there are many choices of materials for light weighting, carbon-fibre-epoxy composites offer the greatest mass reduction for the equivalent stiffness or strength (American Chemistry Council, 2014). Automotive industry is now heavily focused on integrating carbon-fibre-epoxy composites into the vehicle structure.

2.5.5 Glass-fibre-reinforced-polypropylene composite

Polypropylene is a commonly used plastic for automotive purposes, but it has low impact and stiffness properties when compared with metals. Whereas, when reinforced with glass fibres, there are significant improvements in its strength and stiffness by a factor of two or more depending on the percentage of the glass fibres added while still maintaining its low weight (Granta Design Limited, 2015). Glass fibres is the commonly employed reinforcement for polypropylene because of its high availability and low costs (Suresh *et al.,* 2014). The glass fibres are the load-carrying members while the polypropylene transfer stresses between the fibres (Etcheverry *et al.,* 2012).

2.5.6 Nylon-6-nanoclay nanocomposite

Polymer nanocomposites belong to a new class of composite materials formed by filling nanosized materials such as nanofibers, nanoclays, nanotubes, etc. within polymer matrices. The European Commission defines nanomaterial as a material containing particles for which 50% or more of the particles in the number size distribution has one or more external dimensions in the size range 1–100 nm (European Commission, 2011). The molecular level interactions between the nanoparticles and polymer matrices along with the presence of very high nanoparticle-polymer interfacial area play a major role in influencing the physical and mechanical properties of nanocomposites (Rahmat, *et al.*, 2011). In addition to their exhibit excellent mechanical properties, they also display optical, electrical, thermal, magnetic and physicochemical properties (Nanowerk, 2012). Nylon 6 (or polyamide 6) is a polymer possessing good toughness, high tensile strength, elasticity and lustre. It is used for a wide range of products requiring strength. This strength can match with the requirements for car bumpers when reinforced with nanoclay. Nanoclays are nanoparticles of layered mineral silicates. They are naturally occurring inorganic minerals. The most commonly used nanoclay for material reinforcement is montmorrillonite, a 2-to-1 layered smectite clay mineral with a platy structure (Nanocor, 2008).

2.6 Ball Clay

Ball clays are secondary clay that is very rich in kaolinite. It can be obtained in dark brown to black colour because of large amount of impurity content. Ball clay contains kaolinite, mica and quartz. Once ball clay is fired it turns light cream colour from white. Ball clay can also be referred to as plastic clay because of its high plasticity. Stoneware clays and ball clays are alike, but stoneware clays will never give a white product after burning.

As compared to china clays, Ball clays are characterized by higher plasticity, dry strength and dry shrinkage. They most times contain a huge amount of silica, iron and titanium impurities and also chemically impure. These clays, being sedimentary in nature, also contain carbonaceous matter and lignite in agglomerate form (>50Mic) and colloidal form (<2 Mic.). It is believed that the carbonaceous matter within prescribed limit (<2wt %) affects the physical properties of the clay and also increases the unfired strength of clays. However, it increases porosity after firing resulting in decrease in fired strength. It also increases the casting thickness.

2.6.1 Properties of ball clay

The ball clay deposit is sedimentary and consists of numerous strata which frequently vary greatly in physical properties although perhaps not greatly in chemical composition. Ball Clay is Kaolin that has been transported from its primary decomposed parent or igneous rock which were usually granite by nature via glacial displacement making It is a secondary clay and in this process it not only does it gain high organic impurities and iron contaminants, but the material gets ground down into a finer particle size.

2.6.2 Quality specifications of ball clay

Some important quality specifications of ball clays are:

1. Residue / girt content on 45 micron (325 mesh) IS sieve should not be more than 2.0 wt%
2. Particles coarser than 25 micron should be~ 3.0 wt%.
3. Particles finer than 2 microns should be~70 wt% Min.
4. Water of plasticity should be ~ 34 wt % Min.
5. Unfired Strength (MOR) should not be less than 35.0 kg cm^2.
6. Contents of Fe2o3 & TiO2 combined together should not exceed 2.75 wt% and the individual constituents should not be more than 1.5 wt%

2.6.3 Physical properties of ball clay

Main properties include high plasticity due to fine particles which gives high green strength for handling the product at green stage. Requires much more deflocculant to get required fluidity compared to china clay because of fine particles and organic impurities. High Green MOR compared to china clay due to more fine particles. Fired shrinkage is comparatively more due to high loss on ignition and particle size distribution. Green Modulus of Rupture: 65 Kg/cm^2.

1. Water absorption after Firing: Around 10%
2. Ph value: From 6 to 8.
3. % of Dry Shrinkage: 3 to 4 %.
4. % of Fired Shrinkage: 4% to 6%.
5. Residue on 40 mesh: 1% to 3%.
6. Casting rate is comparatively low when compared to china clay in slip condition with same fluidity, viscosity and density.
7. Drying time is slow compared to china clay.

viii. Ball clay should never be tested for colour in the concentrated state, since its density and adsorbed salts give colour intensities which are misleading.

2.6.4 Chemical formula and composition of ball clay.

Chemical formula of ball clay is $Al_2O_3.2SiO_2.2H_2O$

The chemical composition of ball clay varies much from place to place even from one lot to another.

Table 2.3: Chemical Composition of Ball Clay

Mineral	SiO_2	Al_2O_3	MgO	TiO_2	Fe_2O_3	CaO	Na_2O	LOI
Percentage	45 - 55%	30-40%	0.1-0.5 %	5-2 %	0.5-1.5%	0.1-0.5%	0.1-0.6%	14%

Source: Imerys mineral Ltd, cornwall, UK

2.7 Ball clay processing

Ball clays are sold directly from the mine without processing, other than the air drying which may occur under favourable circumstances. Ball clay storage for use but some cases Ball clay is proceed after mining before packing to remove impurities. Steps in the Ball clay processing are

i. Mining.
ii. Sieving.
iii. Settling
iv. Fitter pressing.

i. Mining:

Ball clay is extracted normally by mechanical hydraulic backhoe. Then it will be mixed with water and sent to sieve.

ii. Sieving:

Then the ball clay slurry is passed through series of sieves to remove the impurities. This sieve is passed up to 40 mesh.

iii. Settling:

After sieving the slurry will be passed through series of ziz zak settling to allow clay particles to settle down. In this stage, maximum amount water will be removed.

iv. Filter Pressing:

The slurry from settled tank will be feed into the filter press to remove the water to form cake state clay.

v. Drying and Packing:

The cake form ball clay will be dried in the atmosphere for some time. Then it is packed in bags and transported to customer. Normally Single ball clay is not used in the process because of much varying properties from one delivery to another delivery. So normally two or more ball clay is mixed and used in production process in sanitary ware.

2.8 Calcination of ball clay

One of the most significant ways of improving the properties and value of ball clay is through calcination. Calcination is referred to as a process of heating a substance to below its fusing/melting point, making the substance to loss water. Calcination enhances brightness and whiteness-reduces discolouration of the clay. This increases the roughness of the particles, which can cause some complications during processing because of the degree of aggregation of the particles. The magnitude of these changes depends on the impurities in the clay, period of calcination and the temperature. Consequently, different ball clay will produce different qualities of calcined clay (Chandrasehar, *et al.* 2002). When the main mineral in ball clay (kaolinite) is calcined, it undergoes a sequence of five reactions (Grim, 1968). The first reaction, usually happens between 100 – 150 °C, here, all immersed moisture is removed. (Noble 1980, Taylor 2000). Between 400 and 600 °C the kaolinite undergoes a dehydroxylation reaction, the removal of chemically bonded water, to produce metakaolin, which also has a number of industrial applications, (Drzal, *et al*. 1983).

The exact reaction which takes place is subject to much debate and the only generally accepted theory is that a spinel-type phase forms along with some free silica although the type, its chemical formula and the mechanism of formation are all still under discussion. Above 1050 °C the defect-spinel starts to form hard crystals of mullite and at very high temperatures (above 1100 °C), cristobalite, a carcinogenic material which causes flaws in the refractory material, is formed (Schneider, *et al.* 1994).

Three methods by which ball clay can be calcined are: Soak, Soft, and Flash. Soak calcination implies exposing the ball clay, described as hydrous to high temperatures for a long time in order to be sure that the calcination is complete. The soft calcination method is alike, but it only exposes the clay to high temperatures for a limited amount of time in order to try and minimise the amount of abrasive particles formed. Flash calcination is different from the other two methods in that it involves a quick temperature rise, typically between 900 and 1000 °C within a fraction of a second, achieving a heating rate of 100,000 to 500,000 °C each second. Sealed blisters are formed because steam that evolved from the ball clay cannot escape from the particles. The calcination reaction may also be halted part way through, when temperatures of only 800 °C have been reached and the material is highly reactive.

2.9 Effect of Particle Size On Calcination

The particle size of hydrous ball clay is an important influencing factor on the characteristics of calcined ball clay. Ball clay with a fine particle size has a larger surface area, which means it will be more reactive than coarse Ball clay (Grim, 1968; Noble, 1980; Sugden, 2003). This increased reactivity leads to an increased rate of sintering and mullite formation as well as some initial shrinkage, which results in a decreased porosity (Schneider, *et al*. 1994; Bouchetou, *et al*. 2005). Thermal analysis of Ball clay of different degrees of coarseness shows that, as the particle size decreases, the size of the exothermic reaction that is as a result of the spinel phase reaction, and intensity of the corresponding peak decreases. This is considered to be due to the decrease in crystal phase formation due the fragmented state of the particles (Arens, 1951). The decrease in crystallinity is also accompanied by a characteristic decrease in the onset of dehydroxylation temperature, and a prolonged period of dehydration (Grim, 1962).

There is also an additional effect when the particle size increases, where upon the dehydroxylation and other reactions occur much slower. This phenomenon is found in particles larger than 20 Pm and is thought to occur because the surface area is too small for the dehydroxylation reaction to happen as rapidly as in finer particles and the difference is identifiable using differential thermal analysis (Arens, 1951).

When two ball clay of different particle size, classified as medium and fine were soak calcined and the product examined using electron microscopy, the variations in the product were immediately noticeable. The fine hydrous particles produced a smaller aggregate, with an average size of around 0.7 Pm compared to 1.2 to 2.2 Pm for the medium sized particles. The fine particles, upon calcination, were discovered to have a higher void volume than the medium particles, which had a corresponding effect on the oil absorption of the product. This is due to the increase in porosity; the more pores that are present in the calcined structure, the more oil that can be absorbed (Stewart, 2008).

It has been determined that opacity, the ability of a substance to block light, either through absorption or scattering is improved as particle size decreases. This is an important feature in calcined kaolin as it is primarily used in paint formulation, for which opacity is highly important. This is accompanied by an increase in gloss, another desirable characteristic in the product (Stewart, 2008).

2.10 The Effect of Impurities on Colour After Calcination

2.10.1 Iron

The presence of iron in the clay becomes especially important if the clay is calcined. Heating the clay up to high temperatures causes the iron in the clay to be oxidised from the green/blue Fe^{2+} form, to the red Fe^{3+} form, which can turn the clay a shade of pink. With 'pure' ball clay, good correlations have been found between brightness, yellowness, light absorption coefficients and the analytical iron content at various calcination temperatures from 700^0C upwards, allowing prediction of colour of the final product from the analytical iron content of the feed (Thrale, *et al.* 1990). It has been shown that the brightness of samples varies with the calcination temperature, first decreasing and then improving again as the temperature is raised. The variation derives mainly from changes in light absorption rather than light scattering (Adams, *et al.* 1989). The increase in light absorption (reduction of the brightness) which occurs as the calcination temperature is raised towards 700 °C is due mainly to the conversion of residual surface iron impurities to the intensely coloured red iron oxide, hematite. The decrease in light absorption, on heating above 700 °C is due mainly to one or more solid state reactions involving ancillary materials (Adams, *et al.* 1989).

Due to the complexity of these solid state reactions it is not possible to calculate light absorption or brightness figures for calcined mixtures from the properties of the individual components. Instead, prediction of colour occurs only after laboratory test firing of samples of each calciner feed (Adams, *et al.* 1989). It has been proven that ball clay which has high iron content before beneficiation was favourably comparable, in terms of brightness, with kaolin that had naturally low iron content once both samples had been calcined. This is an important development for the ball clay industry as high quality deposits are used up (Chandrasehar, *et al* 2002).

There is a number of different beneficiation methods, which can be used to remove iron (and other impurities) associated with ball clay. The common techniques include:

i. Size classification for removing coarse minerals and for attaining the specific particle size distribution.
ii. Magnetic separation of the minerals containing iron.
iii. Reductive chemical bleaching to solubilise ferric species and reduce discoloration of remaining ferric sites.
iv. Froth flotation to separate micaceous, graphitic and titanoferrous minerals

The beneficiation steps give a significant added value to raw ball clay, although when the performance of the operation is compared with the overall cost, in most cases, it will not be cost effective (Chandrasehar, *et al* 2002).

The impact of iron in the Ball Clay can be reduced with the use of a reductive atmosphere during calcination and this area has been well-researched. This is due to transformations occurring to the iron species within the clay, with a preference for blue/green coloured Fe^{2+} species, rather than intensely red coloured Fe^{3+} species (Grose, 2004). The use of reductive gases such as carbon monoxide can be replaced by the use of an additive which when burnt under conditions of low oxygen pressure produces the carbon monoxide, e.g. carbon black or ball clay. This gives a comparative colour improvement. Use of a reductive atmosphere, while improving whiteness at a lower calcination temperature, also reduces abrasiveness (Thrale, *et al*.1991).

2.10.2 Organic materials

The effect of organic material on the ball clay depends on the kind and the amount contained within the ball clay material. In general, the organic material occurs in ball clay is several different ways: it may be present as discrete particles of wood, leaf matter, spores etc.; it may be present as organic molecules adsorbed on the surface of the ball clay particles; or it may be intercalated between the silicate layers. The discrete particles may be present in any size, from large chunks easily visible to the naked eye, which can be easily removed through screening in production, to particles of colloidal size, which are much more difficult to remove (Grim,1968).

Ball clay can become contaminated with organic material through both natural and artificial means. During production, dispersants such as polyacrylate are routinely added to the suspension, preventing the ball clay from settling, therefore, making it easier to process through the system. The only chemical reaction undertaken for the hydrous ball clay is that of bleaching, which requires sodium dithionite and acidification, but it is assumed that the entire chemical added is used during the reaction.

Some ball clay production routes, depending on the water source, are affected by the presence of humic acid. This is a particular problem for operations in Devon, where the humic acid enters the water due to plant decay on the slopes surrounding the streams that feed the water circuit used in production. The concentration of the humic acid is highly variable, depending on the season and recent rainfall levels, with levels being particularly high after heavy rain in the winter, when organic matter has begun to decay in large amounts (Dover ,et al.1990).

The effect of the humic acid content on the hydrous kaolin has been determined to be detrimental, with an accompanied increase in feldspar content in the pit wash, leading to an overall concurrent loss in product recovery (Dover,et al.1990). Although the brightness of the hydrous ball clay has been determined to be unaffected, organic materials, which exist as surface contamination, have an effect on the clay colour once calcination has taken place.

Any organics that are present in low temperature calcination have a charring effect, darkening the ball clay and turning it a grey colour. It has, however, been determined that organics are generally removed from the system and fully removed from the ball clay surface by around 800 °C, or possibly lower temperatures, provided that sufficient time is available for complete combustion to occur (Taylor . 2000).

2.11 Fillers

Fillers are solid additives, different from plastics matrices in composition and structure, which are added to polymers to increase bulk or improve properties Fillers have played a major role in meeting these ever more demanding requirements. The introduction of plastic components in automobiles has been rocky. Early attempts to use plastics failed because they lacked strength and weather resistance. Fillers have been responsible for transforming these same plastics to strong durable automotive components. Portable computers have become the truly portable laptop of today due in large part to the lighter, strongly reinforced plastics that are now available. The cases not only look smooth and sleek, they provide shielding from the electromagnetic radiation that used to prevent the use of computers on aircraft in flight. Where filler used to be thought of as a means to lower cost of a plastic part they now contribute to the unique properties that sophisticated users demand. In fact, many fillers now cost more than the polymers that they are added to.

2.12 Theory of The Effect of Fillers

Many naturally occurring functional materials, such as wood, bone, and feathers, are composites consisting of a continuous resinous phase and a discontinuous phase. The first synthetic plastics such as celluloid and Bakelite were also composites. Wood flour was used to reinforce the pioneer phenolic resins and is still used today for the same purpose. According to the American Society for Testing and Materials standard ASTM D- 883, a filler is a relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities or to lower costs, while a reinforced plastic is one with some strength properties greatly superior to those of the base resin resulting from the presence of high-strength fillers embedded in the composition. According to ASTM, plastic laminates are the most common and the strongest type of reinforced plastic. According to one widely accepted definition, fillers are comminuted spherical or spheroidal solids. Glass beads which meet the requirements of this definition are used to reduce mould wear and to improve the quality of moulded parts. The word extender, sometimes used for fillers, is not always appropriate because some fillers are more expensive than the resin.

2.13 Composites

Composites are materials that contain strong fibers embedded in a continuous phase. The fibers are called “reinforcement” fibers and the continuous phase is called the matrix. While the continuous phase can be a metallic alloy or inorganic material, the continuous phase is typically an organic polymer that is termed a “resin.” Because of the use of new fibers and technology, most of the composites discussed in this section are referred to as “space age” and “advanced materials” composites. Composites can be fabricated into almost any shape, and after hardening, they can be machined, painted, etc., as desired. (Raj, *et.al* 1989)

2.14 Applications of Composites

Many of the applications for composite materials involve their (relative) light weight, resistance to weathering and chemicals, and ability to be easily fabricated and machined.

Bulk applications employ composites that are relatively inexpensive. Combinations of rigorous specifications, low volume, specific machining and fabrication specifications, and price comparable to that of alternative materials and solutions allow more expensive specialized composites to be developed and utilized. Applications are increasing but can be roughly divided into seven areas.

2.14.1 Marine craft

One of the largest and oldest applications of composites is in the construction of water going vessels from rowboats, sailboats, racing boats, and motor craft to large seagoing ships.

The use of fresh water-and salt water-resistant composites allowed the boating industry to grow from an almost “mom-and-pop” operation to the use of large boatyards producing craft in an assembly line-like fashion. Most boats are composed of fiberglass and fiberglass/carbon combination composites. Other fibers are also being utilized in the boating industry, including aromatic nylons and fiberglass/aromatic nylon combinations.

2.14.2 Outer space

Because of the large amount of fuel required to propel spacecraft into outer space, weight reduction, offered by composites, is an essential ingredient in the construction of materials utilized in outer space. Some of the solid propellant tanks are made from composites. The tanks are often composed of fiberglass and glass/carbon fiber–containing composites. In fact, the development of S-glass was a result of the space effort. Carbon fibers are employed in the construction of some of the nose fairings. The reusable space shuttles contain various composites. The cargo bay doors are sandwich composites composed of carbon/epoxy/honeycomb materials. The “manipulator arm” used for loading the payload bay is composed of a number of composites including carbon/epoxy composite laminates and aromatic nylon laminates and sandwich materials. Composites are also used for the construction and mounting of mirrors, telescopes, solar panels, and antennae reflectors.

2.14.3 Biomaterials

Bones and skin are relatively light compared with metals. Composite structures can approach the densities of bone and skin and offer necessary inertness and strength to act as body part substitutes.

Power-assisted arms have been made by placing hot-form strips of closed-cell polyethylene (PE) foam over the cast of an arm. Grooves are cut into these strips prior to application and carbon/resin added to the grooves. The resulting product is strong and light, and the cushioned PE strips soften the attachment site of the arm to the living body.

Artificial legs can be fashioned in glass/polyester and filled with polyurethane foam adding strength to the thin-shelled glass/polyester shell. Artificial legs are also made from carbon/ epoxy composite materials. Some of these contain a strong interior core with a soft, flexible skin.

Carbon/epoxy plates are now used in bone surgery, replacing the titanium plates previously employed. Usually a layer of connective tissue forms about the composite plate.

Rejection of composite materials typically does not occur but, as is the case of all biomaterials, compatibility is a major factor. Often lack of biocompatibility has been found to result from impurities (often additives) found in the materials. Removal of these impurities allows these materials to be used.

2.14.4 Sports

Carbon and carbon/glass composites are being used to make advanced material fishing rods, bicycle frames, golf clubs, baseball bats, racquets, skis and ski poles, basketball backboards, etc. These come in one colour-black-because the carbon fibers are black.

Even so, they can be coated with any colour desired.

2.14.5 Automobiles

Composites are being employed in a number of automotive applications. These include racing car bodies as well as "regular" automobiles. Most automobiles have the lower exterior panels composed of rubbery and/or composite materials. Other parts such as drive shafts and leaf springs, antennas, and bumpers in private cars and heavy trucks are being made from composite materials.

2.14.6 Industry

Industrial storage vessels, pipes, reaction vessels, and pumps are now made from composite materials. They offer the needed resistance to corrosion, acids and bases, oils and gases, and salt solutions, as well as the necessary strength and ease of fabrication to allow their continued adoption as a major industrial building material.

2.14.7 Aerospace

The Gulf War spotlighted the use of composite materials in new-age aircraft. The bodies of both the Stealth fighter and bomber are mainly carbon composites. The versatility is apparent when one realizes that the Gossamer Albatross, the first plane to cross the English Channel with human power, consisted largely of composite materials, including a carbon/ epoxy and aromatic nylon composite body and propellers containing a carbon composite core.

The increase in use of composite materials by the aerospace industry is generally due to their outstanding strength and resistance to weathering and fraction and their light weight, allowing fuel reduction savings. Succeeding families of Boeing aircraft have used ever greater amounts of fiberglass composite material in their manufacture, from about 20 square yards for the 707, to 200 square yards for the 727, to 300 square yards for the 737 and over 1000 square yards for the 747. This amount is increased again in the Boeing 767 and includes other structural applications of other space-age composites. Thus, the Boeing 767 uses carbon/aromatic nylon/epoxy landing gear doors and wing-to-body fairings. As noted above, most applications of composites in the aerospace industry involve decreased weight, resulting in increased (potential) payloads and decreased fuel consumption. Interestingly, the lack of even limited flexibility for many composites limits their use (currently) for large commercial aircraft where normal wing "flapping" amplitudes may be several feet during a flight. Even so, composite use is increasing in the construction of small aircraft such as the McDonnell Douglas F-18, where roughly 50% of the outer body surface is composite, with the remainder being largely a mixture of titanium, aluminium, and steel. Other areas of increased composite use include helicopter blades (giving about a two fold increase in life expectancy compared to metal blades) and jet engines (e.g., turbo fans, cowling, container rings).

In its most basic a composite materials is one which is composed of at least two element working together to produce materials properties that are different to the properties to the properties of those elements on their own. In practice, most composite's consist of a bulk materials (the matrix), and a reinforcement of some kind, added primarily to increases the strength and stuffiness of the matrix.

2.15 Filler Dispersion

The primary requirement for obtaining a satisfactory performance from short-filler composites, including cellulose-based composites, is good filler dispersion in the polymer matrix. Good dispersion implies that the filler are separated from each other (i.e. there are no clumps and agglomerates), and each filler is surrounded by the matrix. Insufficient filler dispersion, on the other hand, results in an inhomogeneous mixture of resin-rich areas and filler-rich areas. This is undesirable because the resin-rich areas are weak and the filler-rich areas (i.e., clumps) are susceptible to micro-cracking. Micro-cracks contribute to inferior mechanical properties of composites. It is therefore important to ensure homogeneous filler dispersion in order to achieve maximum strength and performance of the composite materials. There are two major factors that affect the extent of filler dispersion, filler-filler interaction such as strong hydrogen bonding between the filler, and filler length. The same factors also account for the tendency for fillers, such as cellulose fillers, to agglomerate during mixing. The filler length used in the preparation of composites is critical. It should not be too long; otherwise, the filler may get entangled with each other. This will cause problems with filler dispersion. If fillers are too short, the stress transfer area will be too small for the fillers to offer effective reinforcement. According to Derringer (1971), commercially available fillers such as nylon, rayon, and polyester need to be cut into lengths, of approximately 0.4 mm for best dispersion. As mentioned before, one of the major drawbacks of using cellulose fillers as reinforcement is because of their poor dispersion characteristics in many thermoplastic melts, such as polypropylene and polystyrene, due to their hydrophilic nature. Several methods have been suggested and described in the literature to overcome this problem. Among them are filler surface modifications, use of dispersing agents such as stearic acid, and pre-treatments such as acetylation. Filler dispersion can also be improved with increased shear force and mixing time. A careful selection of initial filler lengths, processing aids, processing techniques as well as processing conditions, then is necessary in order to produce high performance composites. Raj and Kolkata (1989) investigated the influence of using various dispersing aids (stearic acid and mineral oil) and a coupling agent (maleate ethylene) in cellulose filler reinforced polypropylene composites. Tensile strength and modulus of the composites studied were found to increase with filler content when either stearic acid or mineral oil (1% by weight of fiber) were added as processing aids during the compounding. The properties also were found to be affected by the amount of processing aid used. Maximum increases in the properties were observed when the processing aid was added in 1% concentration (by weight of fiber). A further increase in the amount of processing aid caused the properties to decline dramatically. Stearic acid was found to perform better in improving the filler dispersion compared to mineral oil.

Good filler dispersion is generally the ultimate objective of any mixing process. Various mixers are available to mix short filler in the thermoplastics such as extruders, plasticorder, injection molding machines and kneaders. Different mixing techniques, however, do not produce composites with the same degree of filler dispersion. Woodhams, *et al.* (1990) and Myers, *et al* (1992) used a thermo-kinetic mixer to mix cellulose filler within thermoplastic and found the techniques effective in dispersing the cellulose filler within thermoplastic matrices. The effectiveness of the technique was then confirmed by Sanadi, *et al.* (1994). Pereira, *et al* (1997).

2.16 Filler-Matrix Adhesion

Filler to mix adhesion plays a very important role in the reinforcement of composites with short fillers. During loading, loads are not applied directly to the filler but to the matrix. To have composites with excellent mechanical properties (ultimate strength but toughness), the load must be transferred effectively from the matrix to the fillers. This requires good interaction as well as adhesion between the filler and the matrix, i.e. strong and efficient filler-matrix interface. This can be controlled by either surface treatment applied to the filler or by the use of additives such as coupling agents.

Many studies have been done on various composite systems either to improve the efficiency of the interface in transferring stress or understand the mechanism involved. Poor compatibility and dispersability in hydrophobic thermoplastics leads to poor wetting and interfacial bonding between the fillers and the matrix resulting in composites with poor mechanical properties. These problems, however, can potentially be overcome. The use of coupling agents, polymer coating materials, fiber pre-treatments and chemical grafts, have been reported to improve wetting as well as interfacial bonding between cellulose fillers and thermoplastic matrices. This is due to improved filler-matrix adhesion as well as filler dispersion.

Childress, *et al* (1993) investigated the effectiveness of several additives in enhancing mechanical properties of wood filler and high-density polyethylene composites. Thomas, *et al.* (1996) reinforced polystyrene with benzoylated sisal fillers. The results revealed better compatibility between treated cellulose fillers and the polystyrene matrix, and this resulted in enhanced tensile properties of the resulting composite. SEM micrographs revealed evidence of improved filler wetting and filler-matrix adhesion between the components. These improvements were attributed to the similarity between the phenyl-structure present in both benzoylated sisals fillers and polystyrene, which makes them thermodynamically compatible with each other.

2.17 Filler Aspect Ratio

Filler aspect ratio, i.e. the length to diameter ratio of filler, is a critical parameter in a composite. An expression relating critical filler aspect ratio ($1e / d$) to interfacial shear stress (τy) has been proposed by Cox, on the basis of shear-lag analysis.

$$1e / d=\bar{\alpha}fu/2\tau y \qquad (2.1)$$

Where:

Le = critical filler length

D =diameter of filler

$\bar{\alpha}fu$ =filler ultimate strength in tension

τy = interfacial stress

At control $\bar{\alpha}fu$, the equation reveals an inverse relationship between Le /d and ty, where Le /d become short (low) as ty, i.e. Interfacial shear stress (transfer) becomes efficient (high). Internal shear stress, which influences fiber aspect ratio, can be varied by modifying the filler-matrix interface by using chemicals such as coating agents.

For each short-filler composite system, there is a critical filler aspect ratio that may be defined as the minimum filler aspect ratio in which the maximum allowable filler stress can be achieved for a given load. This parameter is determined not only by filler and matrix properties, but also by the quality of the filler/matrix interface .Load is transferred from the filler to the matrix by shear along the filler/matrix interface. For maximum reinforcement, the filler aspect ratio of any composite system should be above its critical value. This will ensure maximum stress transfer to the fillers before the composite fails .If the filler aspect ratio is lower than its critical value, insufficient stress will be transferred and reinforcement by the fillers will be inefficient, i.e., the fillers are not loaded to their maximum stress value. By contrast, if the filler aspect ratio is too high, the fillers may get entangled during mixing causing problems with filler dispersion. During processing, fillers, such as glass and carbon fillers, are often broken into smaller fragment; this may potentially make them too short to be useful for reinforcement. However, cellulose fillers are flexible, and resistance to fracture during processing can be expected. This enables the fillers to maintain a desirable filler aspect ratio after processing. Several investigators have suggested that an aspect ratio in the range of 100-200 after processing is essential for high performance short-fiber composites.

2.18 Filler Orientation

Filler orientation is another important parameter that influences the mechanical behaviour of short-filler composites. This is because the fillers in such composites are rarely oriented in a single direction, which is necessary for the fibers to offer maximum reinforcement effects. As a result, the degree of reinforcement in a short-filler composite is found to be strongly dependent on the orientation of each individual filler with respect to the loading axis. Changes in filler orientation take place continuously and progressively during the processing of short-filler composites. The changes are related in a complex way to the geometrical properties of the fillers, the visco-elastic properties of the matrix, and the change in shape of the material which is produced by the processing operation. In these operations, the polymers melt will undergo both elongation or extensional flow and shear flow.

Thomas, *et al.* (1996) reinforced polystyrene with benzoylated sisal fillers. The influence of fiber length, filler content as well as filler orientation on the composite produced was evaluated. Randomly oriented composite specimens were prepared by injection moulding while the unit-directionally oriented compression moulding. The specimens were then observed under an optical stereomicroscope to confirm orientation. A longitudinally oriented composite (the fillers are oriented parallel to the test direction) was found to show the best mechanical properties. This was followed by randomly and transversely oriented composites i.e. the fillers are oriented transverse to the test direction.

2.19 Filler Volume Fraction

Like other composite systems, the properties of short-filler composites are also crucially determined by fiber concentration. Variation of composite properties, particular tensile strength, with filler content can be predicted by using several models such as the Rule of Mixtures', which involves extrapolation of matrix and filler strength to filler volume fractions of 0 and 1. At low filler volume fraction, a drastic decrease in tensile strength is usually observed. This has been explained with dilution of the matrix and introduction of flaws at the filler ends where high stress concentrations occur, causing the bond between filler and matrix to break. At high filler volume fraction, the matrix is sufficiently retrained and the stress is more evenly distributed. This results in the reinforcement effect outweighing the dilution effect. As the volume fraction of fillers is increased to a higher level, the tensile properties gradually improve to give strength higher than that of matrix. The corresponding filler volume fraction in which the strength properties of the composite cease to decline with filler addition, and begin to improve, is known as the optimum or critical filler volume fraction , $\mathbf{V}_{crit}$.

For short-filler composites to perform well during service, the matrix must be loaded with fillers beyond this critical value. At high filler volume fraction, the strength again decreases due to insufficient matrix material.

2.20 Processing of Reinforced Plastics

The processing of filler/thermoplastic composites involves heating the thermoplastic to above its melting point and providing sufficient shearing agitation to ensure intimate mixing between filler and plastic matrix. The heating and shearing action may be accomplished by a number of different types of plastic processing equipment.

The plastic industry was reluctant to use wood filler as filler because of its low bulk density, low thermal stability and tendency to absorb moisture. The choice of plastic to be used is based on its inherent properties, product need, availability, low cost and the manufacturer's familiarity with the material. The manufacture of thermoplastic composites is often a two-step process. The first stage involves mixing the raw materials and dispersing the filler additives in the molten polymer matrix through the use of batch or continuous mixers. The second stage is to form the compounded material into a product. The conventional techniques of natural fibre reinforced composites include:

i. Injection moulding
ii. Compression moulding
iii. Extrusion
iv. Thermoforming
v. Reaction injection moulding (RIM) for foamed parts.

Fabrication to ensure reliable properties in composite parts and structures, particularly over the long range of their service life, can present significant challenges because of the presence of two or more types of materials. The matrix and the reinforcing have very different properties and characteristics and consequently have different responses to the method of processing.

Polymer-matrix composites have a complex structure; hence they require special methods to shape them into consumer and industrial products. As a result, several innovative techniques have been developed to manufacture both large and small parts, particularly by moulding, forming, cutting and assembly. The several methods involved in manufacturing reinforced plastics and the time and care required, makes the processing cost very substantial and are not competitive with traditional materials and shapes (Serope K and Seven S.,) Careful inspection and testing of reinforced plastic is essential in critical application in order to ensure that good bonding between the reinforcing fillers and the matrix has obtained throughout the world structure.

2.20.1 Extrusion

Extrusion of natural reinforced polymer composites for the automotive industry is the most method and has been used for more than two decades. The extrusion process lends itself to processing the high velocity of the molten natural filler reinforced composites lends and shaping the long, continuous profiles common to building materials. Typical blending involves shear mixing the constituents at temperatures above softening point of the plastics. Moisture can be removed from the composites before processing, during a separate compounding step or by using the first part of an extruder as a dryer in some in-line process. In the extrusion of process of rubber, the compound including polymers, various types of additives and fills like curing agents, antioxidants, pigments are fed into the extruder. The extruder typically consists of rotating screw insides a closely fitted heated barrel. The primary purpose of the extruder is to do three things,

a) Soften
b) Mix
c) Pressurize the rubber as it is fed continuously to the die at extruder exit.

The die is a sort of metal disk that has a machined opening in the desired shape of the part that needs to be extruded. The rubber already softened by heating is then forced by the rotating screw through the die opening into the shape of the profile cut in the die. T typical phenomenon called die swell takes place as the rubber shape leaves the die.

Because of this the part cross-section becomes larger than the die cross-section. The part cross-section depending on the material may rise up to several folds over the die. Subsequently the processes of vulcanization or curing takes place as the last step in the extrusion process. This aid the rubber extruded profiles maintain its shape and acquire necessary physical properties.

2.20.2 Compression Moulding

Compression moulding is process in which a compound is squeezed into a pre-heated mould taking a shape of the method cavity and performing curing due to heat and pressure applied to the material. It consists of placing the composites materials between two moulds, then applying pressure. The moulds may either be at room temperature or heated to accelerate hardening of the part. Compression moulding may be a secondary operation after extrusion. I n this cases the extruder is a semi-finished product in the form of a pellet is then compressed to obtain the desired product.

Compression moulding process involves the following steps:

i. A pre-weighted amount of the compound is placed into the lower half of the mould. The compound may be in form of putty-like masses or pre-formed blanks.

ii. The upper half of the mould moves downwards, pressing on the compound and forcing it to fill the mould cavity. The mould, equipped with a heating system, provides curing (cross-linking) of the compound.

iii. The mould is opened and the part is removed.

In compression moulding there are six important considerations that an engineer should bear in mind.

a) Determining the proper amount of material.

b) Determining the minimum amount of energy required to heat the material.

c) Determining the minimum time required to heat the material.

d) Determining the appropriate heating technique.
e) Predicting the required force, to ensure that shot attains the proper shape.
f) Designing the mold for rapid cooling after the material has been compressed into the mould.

2.20.3 Transfer Moulding.

Transfer moulding is a process in which a pre-weighed amount of a compound is preheated in a separate chamber (transfer pot) and then forced into a preheated mould through a sprue, taking a shape of the mould cavity and performing curing due to heat and pressure applied to the material.

Transfer/injection moulding is an automated operation that combines compression moulding, injection moulding and transfer moulding processes. The method uses a split mould and third plate equipped with a plunger mounted in a hydraulic press.

The method of combines features of both compression moulding (hydraulic pressing) and injection moulding (ram-plunger and filling the mold through a sprue).

The transfer of moulding process involves the following steps:

i. A pre-weighted amount of a compound is placed into the transfer pot. The compound from putty-like masses or pre-formed blanks. The compound is heated in the pot where the material softens.
ii. The plunger, mounted on the top plate, moves downwards, pressing on the materials and forcing it to fill the mold cavity through the sprue. The mould, equipped with a heating system, provides curing (crossing-linking) of the compound.
iii. The mold is opened, and parts are removed.
iv. The scrap left on left on the pot bottom (cull), in the sprue and in the channels is removed. Scrap of vulcanized rubber is not recyclable.

The transfer moulding cycle time is shorter than compression moulding cycle but longer than the injection moulding cycle. The method is capable to produce more complicated shapes than compression moulding but not as complicated as injection moulding. Transfer moulding is suitable for moulding with ceramic or metallic inserts which are placed in the mould cavity. When the heated compound fills the mould it forms bonding with the insert surface.

This process has the good surface finish, dimensional stability and mechanical properties obtained in compression moulding with automation capability and low cost-obtained in injection moulding.

2.20.4 Injection Moulding

Injection moulding is similar to hot-chamber die casting. The pellets or granules are fed into the heated cylinder and the melt is forced into the mould either by a hydraulic plunger or by the rotating screw system of an extender. The pressures developed ranged from 70 to 200 MPs. Moulds in use include two-plate mould, three-plate mould, and hot-runner (Runnerless) mould. For thermoplastics, the moulds are kept relatively cool at about 90ºC, while for thermosets, the moulds are heated to about 200ºC.

Injection moulding is a versatile, high-rate production process which permits good dimensional control. Typical cycles time range from 5 to 60 seconds, although thermosetting materials may take several minutes. Injection moulding may be modified to form components with a combination of various colours and shapes. This process is called multi-component or co-injection moulding moulding and is employed in moulding of rear-light covers for automobiles. Yet another modification is the insert moulding in which metallic components such as screws, pins and strips are placed at designated positions in the mould cavity prior to injection and then they become an integral part of the moulded product.

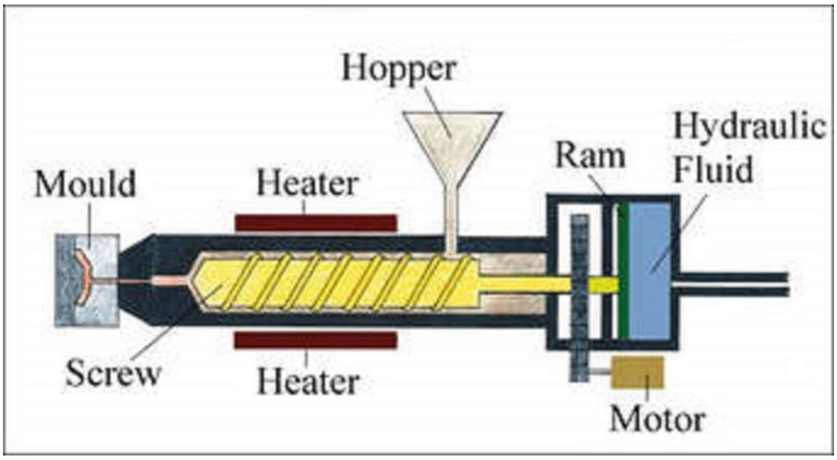


Figure 2.1: Injection Moulding Machine

The injection system consists of a hopper, a reciprocating screw and barrel assembly and an injection nozzle, as shown in Figure 1. This system confines and transports the plastic as it progresses through the feeding, compressing, degassing, melting, injection, and packing stages.

i.The Hopper:

Thermoplastic material is supplied to the moulder in the form of small pellets. The hopper on the injection moulding machine holds these pellets.

ii.The Barrel:

As shown in Figure 1, the barrel of the injection moulding machine supports the reciprocating plasticizing screw. It is heated by electric heater bands.

iii.The Reciprocating Screw:

The reciprocating screw is used to compress, melt and convey the material. The reciprocating screw consists of three zones;

a) The feeding zone

b) The compressing (or transition) zone

c) The metering zone

While the outside diameter of the screw remains constant, the depth of the flights on the reciprocating screw decreases from the feed zone to the beginning of the metering zone. These flights compress the material against the inside diameter of the barrel, which creates viscous (shear) heat. This shear heat is mainly responsible for melting the material in the molten state. Typically, a moulding machine can have three or more heater bands or zones with different temperature setting.

iv.The Nozzle:

The nozzle connects the sprue bushing of the mold and forms a seal between the barrel and the mould. The temperature of the nozzle should be set to the material's melt temperature or just below it, depending on the recommendation of the material supplier. When the barrel is in its full forward processing position, the radius of the nozzle should nest and seal in the concave radius in the sprue bushing with a locating ring. During purging of the barrel, the barrel backs out from the sprue, so the purging compound, can free fall from the nozzle.

v.Mould System

A mold system is an assembly of platens and molding plates typically made of tool steel. The mould system shapes the plastics inside the mould cavity (or matrix of cavities) and ejects the moulded parts(s). The stationary platen is attached to the barrel side of the machine and is connected to the moving platen by the bars. The cavity plate is generally mounted on the stationary platen and houses the injection nozzle. The core plate moves with the moving platen guided by the tie bars. Occasionally, the cavity plate is mounted to the moving platen and the core plate and a hydraulic knock-out (ejector) system is mounted to the stationary platen. The mould system consist of tie bars, stationary and moving platens, as well as moulding plates (bases) that house the cavity, sprue and runner systems, ejector pins, and cooling channels. The mould is essentially a heat exchanger in which the molten thermoplastic solidifies to the desired shape and dimensional details defined by the cavity.

vi. **Cooling Channels (Circuits)**

Cooling channels are passenger ways located within the body of a mould, through which a cooling medium (typically water, steam, or oil) circulates. Their function is the regulation of temperature on the mould surface. Cooling channels can also be combined with other temperature control devices, like baffles, bubblers, and thermal pins or heat pipes.

vii. **Hydraulic System**

The hydraulic system on the injection moulding machine provides the power open and close the mold, build and hold the clamping tonnage, turn the reciprocating screw, and energize ejection pins and moving mold cores. A number of hydraulic components are required to provide this power which includes pumps, valves, hydraulic motors, hydraulic fittings, hydraulic tubing, and hydraulic reservoirs.

viii. Control System

The control system provides consistency and repeatability in machine operation. It monitors and controls the processing parameters, including the temperature, pressure, injection speed, screw speed and position, and hydraulic position. The process control has a direct impact on the final part quality and the economics of process. Process control systems can range from a simple relay on/off control to an extremely sophisticated microprocessor-based, close-loop control.

ix. Clamping System

The clamping system opens and closes the mold, supports and carries the constituent parts of mold, and generates sufficient force to prevent the mold from opening.

Clamping force can be generated by a mechanical (toggle) lock, hydraulic lock, or a combination of the two basic types.

x.Molded System

A typical moulded system consists of the delivery system and the moulded part(s)

a) The Delivery System

The delivery system, which provides passage for the molten plastic from the machine nozzle to the part cavity, generally includes:

i. A sprue
ii. Cold slug wells
iii. A main runner
iv. Branch runners
v. Gates

The delivery system design has a great influence on filling pattern and thus the quality of the moulded part.

b) Cold Runners

After moulding, the cold-runner delivery system is trimmed off and recycled. Therefore, the deliver y system is normally designed to consume minimum material, while maintaining the function of delivering molten plastic to the cavity in a desirable pattern.

c) Hot Runner

The hot runner (or runnerless) moulding process keeps the runners not in order to maintain the plastic in a molten state at all times. Since the hot-runner system is not removed from the mold with the molded part, it saves material and eliminates the secondary trimming process.

Much of the initial research has involved the use of extruders and thermo-kinetic mixers. In thermo-kinetic mixers, unique processing equipment that may be suitable for blending lignocelluloses with commodity plastics, the shearing action of the high speed impeller blades generates sufficient heat to both melt and mix the blend. But the commercialization of fiber/plastic composites has developed almost exclusively with the utilization of plastic extrusion technology.

Although both heat and agitation are necessary for compounding thermoplastics and fibers, both the heat and the shearing action can have detrimental effects on the incorporated fibers. Although heating to above melting point of the thermoplastic may be necessary, exposure of the fibre to the pyrolytic, degrading effects of heat should be minimized. This usually requires processing at temperatures lower than those conventionally used with neat polymers or with inorganic-filled polymers. Because of the high temperatures employed, and the moisture sensitivity of cellulosic fillers, pre-drying of fillers prior to compounding (or other control methods) is necessary.

The shearing action which is necessary for intimate mixing of filler/ thermoplastic composites also has detrimental effects on the filler-length distribution. Aggressive sharing elements in an extruder can effectively change the reinforcing characteristics of filler to those of non-reinforcing filler. Furthermore, shearing tends to expose new surface of the filler in melt blending techniques, and the level of shearing will determine whether the exposed surface is rich in lignin or hemi-cellulose.

Maximum reinforcement is gained by incorporating large volume fraction of high modulus fillers in matrices. The requirement for a high volume fraction of fillers poses practical processing difficulties. Although the maximum volume of perfectly aligned cylindrical fillers that can be packed into a composite is theoretically about 91%, in practice lower limits are reached because of the inability of matrix and infiltrate the fillers. Flexible fillers twist and rotate in many complex ways and each filler effectively occupies an extended volume from which other fillers are excluded. During processing, when two fillers approach, collisions may occur, but filler need not actually touch in order to affect each other's paths. At very low filler fractions, the whole of the suspension is occupied, and no free rotation is possible. Interaction between fillers is evidenced in the final composite in two ways: filler alignment and filler clumping.

As the concentration of fillers increases, their rotations are affected, and fillers even at low concentration under shear will assume a preferred orientation in the direction of shear. This orientation becomes more apparent as the filler content increases as the result of the multiple collisions and correlated orientations between fibers. At higher concentrations, filler clumping occurs.

The performance (mechanical and physical properties) of natural filler-reinforced composites depends to a great extent on the following factors:

i. Type of reinforcing material and the matrix.
ii. The shape of the reinforcing fillers.
iii. The orientation of the fillers.
iv. The length of the fillers.
v. The volume fraction of the reinforcement.
vi. The presence and effect of other additives.
vii. Interaction between these materials.
viii. The processing variables and techniques.
ix. The product design.
x. The service environment.

The key idea behind composites is that the properties of composites are determined at least to a large extent, by the simple rule of mixture.

$$PRP = P_F V_F + P_m V_m \qquad (2.2)$$

Where P=property

V= Volume fraction

RP= Reinforced plastic

F=fibre/filler

M=polymer matrix.

This implies that the properties of properties of composites are highly dependent on the properties of their constituents. The attractiveness comes from the fact that you can use very high performance fillers in terms of mechanical strength in a lower strength in lower strength matrix.

In natural filler reinforced composites, short fillers are less effective than long fillers and their properties are strongly influenced by temperature and the time under load. A short filler is one in which the mechanical properties improve as a result of increasing the average filler length, if no such improvement occurs, it is called a long filler.

Natural filler-reinforced composite is an engineered material. As a result, a reinforced plastic product can be given optimum configuration for a specific service condition, for example, if a product is to subject to forces in different directions such as in thin walled pressurized vessels, then different directions such as in thin walled pressurized vessels, then

- The filler can be criss-crossed in the matrix or
- Layers of fillers oriented in different direction can be built up into a laminate having improved properties in more than one direction.

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 Materials and Equipment Used

3.1.1 Materials used

- Virgin high density polyethylene (HDPE) pellets.
- Raw Ball clay
- Calcined Ball clay

3.1.2 Equipment

- Electronic weighing machine.
- Injection moulding machine.
- Universal testing machine, model:TUE-C 100 serial no: 2010/32
- Carbolite GPC1300 Furnace
- Mechanical screen/sieves.

3.2 Collection and Preparation of The Materials

Ball clay was collected from Agaie, Niger State. Before being characterized, the sample were crushed using Thomas grounding machine to break up the agglomerates. The samples where further milled in a cascading ball mill to obtain fine particles. The Ball clay was sieved with a screen of mesh size 850 µm.

High Density Polyethylene (HDPE) was used in this study as the polymer matrix. This HDPE pellet was sourced from Indorama Eleme Petrochemical. Table 3.1 below show the mechanical properties of the density polyethyelene purchased from Indorama Eleme Petrochemical. This data was extracted from the technical data sheet of the purchased HDPE.

Tables 3.2 and 3.5 shows the mass of HDPE, mass of raw ball clay and calcined ball clay used to form the composite. Samples A_1 and B_1 constitute 100% HDPE, while samples A_2 constitute 950g of HDPE and 50g of Raw ball clay which represents 5% weight fraction.

TABLE 3.1 Typical Characteristics Of High Density Polyethylene (Source: Indorama Eleme Petrochemicals Technical Data Sheet)

PROPERTY	TEST METHOD	UNIT	VALUE
Melt Flow Index ($190^0C/2.16$ kg)	ASTM D 1238	gm/10 min.	4.5
Density	ASTM D 792	gm/cm3	0.956
Tensile Strength at Yield	ASTM D 638	MPa	29
Elongation at Break	ASTM D 638	%	850
Flexural Yield Strength	ASTM D 790	MPa	31
Flexural Modulus	ASTM D 790	MPa	900
Impact Strength	ASTM D 256	J/m	70
Vicat Softening Point	ASTM D 1525	^0C	128
Hardness	ASTM D 2240	Shore D	69

Table 3.2: Mass of High Density Polyethylene (HDPE) and Raw Ball Clay Composites**.**

Sample	Mass of virgin HDPE used (g)	Mass Raw Ball Clay used(g)	%weight fraction of Raw Ball clay
A_1	1000	0	0
A_2	950	50	5
A_3	900	100	10
A_4	850	150	15
A_5	800	200	20
A_6	750	250	25
A_7	700	300	30

B. Raw ball clay

This was sourced at Agaie, Niger State, Nigeria and the chemical composition of the Ball clay was determined using silicate method. To remove impurities like plant materials, the raw ball clay was sieved with a screen of mesh size 850µm.The chemical composition of raw ball clay is showed in table 3.3 below. The Al_2O_3 and SiO_2 content in the samples are 30.33 % and 47.65 % respectively. The amount of alkaline oxides (K2O+Na2O) that acting as flux materials is about 1.07%. The amount of CaO and MgO is low and this indicate the absence of carbonates. The relatively high loss on ignition (average about 4.87%) associated with high SiO2 and low Al2O3 contents are due to the significant content of quartz, low amount of clay minerals and high amount of carbonaceous material in the samples.

C. Calcination of ball clay

Laboratory calcination was carried out using a Carbolite GPC130 controlled with a Eurotherm 2416. The kiln has a heating area of 0.32 m by 0.43 m, a height of 0.25 m and is heated with APM (a nickel, chromium and aluminium alloy) wire heating elements which are located on the two sides of the kiln.

At the base of the kiln, there is a refractory board which is 0.26 m by 0.33 m wide and 0.02 m thick. This is located in the centre of the kiln base and supports all samples during the heating/cooling cycle. Prior to calcination; the empty crucible was weighed before the hydrous ball clay was carefully poured into the crucible, using a 50 ml plastic scoop, taking care to not compress the powder in doing so. The crucible was then weighed for a second time and the value recorded. This was done to ensure correct sample identification following the calcination and also to determine the loss on ignition, with the addition of fired weight data. This was a simple method of guaranteeing that a reaction had actually taken place.

The method of calcination used here is soak calcination. Soak calcining involves placing a powder filled crucible into a furnace when it is cold and leaving it inside until the temperature reaches the required level, allowing it to dwell at 700 °C temperature for the required length of time, before letting it cool at a natural rate, before the sample is removed.

Table 3.3: Mass of High Density Polyethylene and Calcined Ball Clay Composites.

Sample	Mass of virgin HDPE used (g)	Mass Raw Calcined Clay used(g)	% weight fraction calcined Ball Clay
B_1	1000	0	0
B_2	950	50	5
B_3	900	100	10
B_4	850	150	15
B_5	800	200	20
B_6	750	250	25
B_7	700	300	30

3.3 Scanning Electron Microscope (Sem) Of Raw Ball Clay Calcined Ball Clay

The Raw ball clay and calcined ball clay were subjected to scanning electron microscope (SEM) to obtain more understanding on the structures and size distributions of the samples. The Figures 4.1, and 4.4 show the SEM structure of the Ball clay and calcined ball clay.

The morphology of the samples was determined by scanning electron microscope (SEM) and the elemental composition was determined by Energy Dispersive X-ray Dispersion (EDX).

The Calcined Ball clay shows larger particle sizes and many irregular shapes which increases the tensile strength at yield and impact strength. The SEM images show that raw ball clay has smaller particle size than calcined ball clay.

3.4 X-Ray Diffraction (Xrd) Pattern

The X-ray diffraction (XRD) analysis was carried out to investigate the phase composition, crystalline structure and the degree of disorderliness of raw ball clay and calcined ball clay. The result from these XRD patterns are presented in Figure 4.3 and 4.5. The X-ray diffraction was determined using the Siemens D500 X-Ray Diffractometer System and the value points were obtained using (STOE WinX^{POW}2.10) software.

The X-ray pattern is presented in Figure 4.3, it can be seen that a wide diffraction feature appears in the 2theta range at 11^{o} 25^{o} 27$^{o.}$ The result shows a disordered structure of Silicon content and some of the sharp peaks indicates the presence of Aluminium, Iron and Silver.

3.5 Composite Processing

In this research work, Raw and calcined ball clay are the fillers used to form reinforced composite with virgin high density polyethylene. The composite was formed at springboard Research Laboratory Awka, Nigeria. The high density polyethylene was mixed with raw ball and calcined filler at various composition. The mixture was fed into an injection moulding machine. The operating pressure and temperature of the injection moulding machine was 10 MPa and 160 ^{0}C respectively, and the process time for each sample is 4 mins. The raw materials to be compounded are fed into the injection moulding machine through the hopper. In the cylinder of the machine, the resin is heated to plasticize is ready for injection into the mould. This plasticized material enters the mould through the nozzle which is screwed to the end of the cylinder. At the end of the moulding cycle, the mould opens and the moulding is rejected. The results of the Impact strength test and tensile strength at yield are shown in tables 4.1 and 4.2. Figure 3.1 shows the various stages of this research.

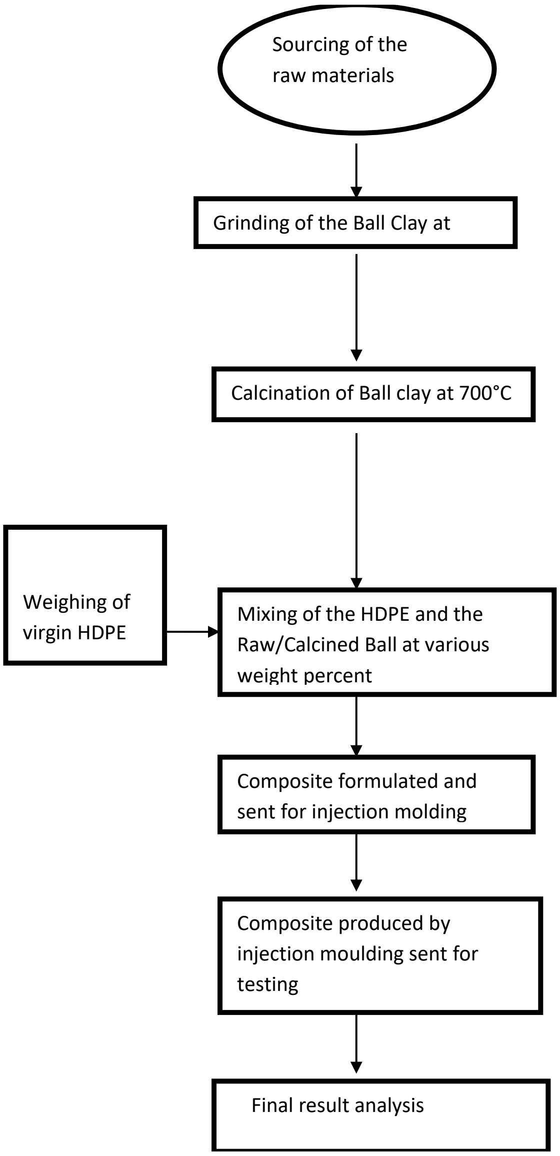


Fig 3.1 Simple Flow Chart Showing the Preparation of Various Reinforced Polyethylene-Filler Composites from Raw Material Testing to Result Analysis.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter contains results obtained from the tensile strength at yield and impact strength of Raw Ball clay-HDPE composite and Calcined Ball clay-HDPE composite. The tensile strength at yield and impact strength test was performed at standard organization of Nigeria laboratory Enugu State.

4.1 Scanning Electron Microscope (Sem) Of Raw Ball Clay Calcined Ball Clay.

The SEM images for calcined and raw ball clay shows larger particle sizes and small particle size. According to Grim (1962) calcination of clay increases the crystallinity of the clay and large particle increases the tensile strength at yield and impact strength of the composite. This agrees with Grim (1962) that calcination of ball clay alters the morphology of ball clay. According to Stewart (2008), raw ball clay upon calcination, were discovered to have a higher void volume . This is due to the increase in porosity - larger particle clay sizes.

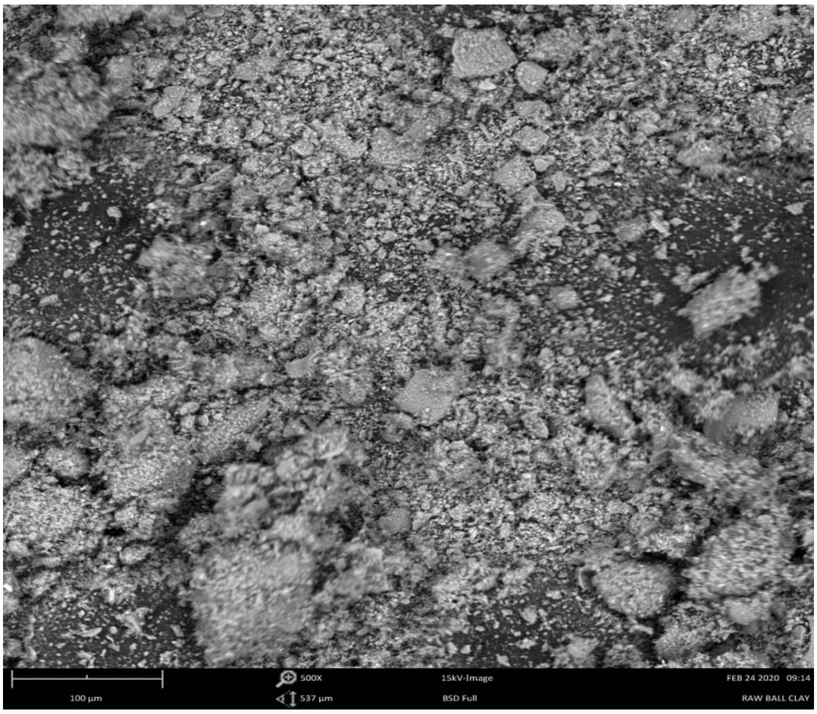


Figure 4.1: SEM Image of Raw Ball Clay

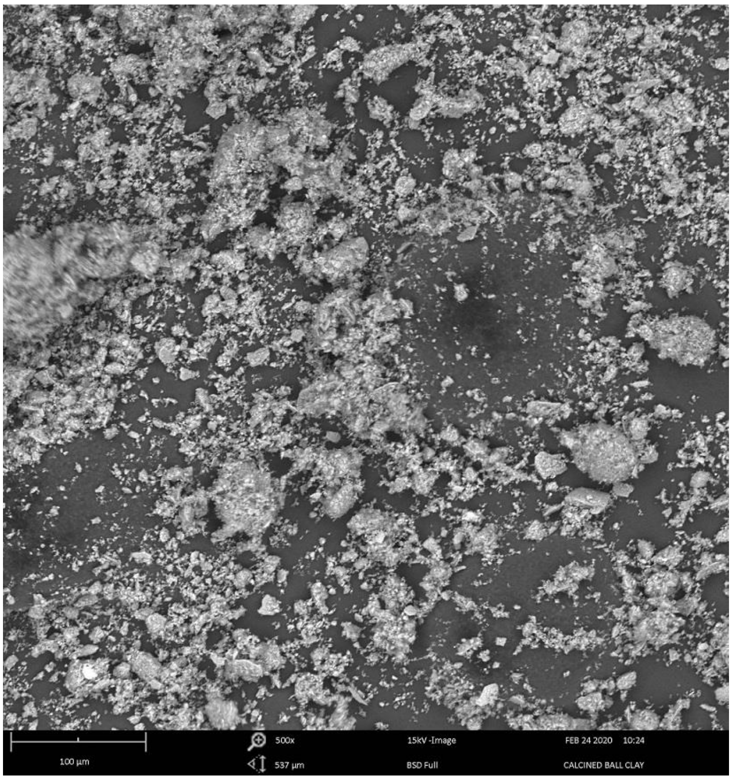


Figure 4.2: SEM Image of Calcined Ball Clay

4.2 X-Ray Diffraction (XRD) And EDX Patterns

The X-ray pattern is presented in Figure 4.3, it can be seen that a wide diffraction feature appears in the 2theta range at 11^{o} 25^{o} $27^{o.}$ The result shows a disordered structure of Silicon content and some of the sharp peaks indicates the presence of Aluminium, Iron and Silver.

The XRD patterns for the Raw ball clay and Calcined ball clay shows the dominant presence of Sio$_2$ and some trace of S, Ti and Fe. The EDX pattern presented in figure 4.4 and 4.6 for Raw ball clay and Calcined ball clay respectively, confirms the presence of silicon and aluminium as major elemental composition. The XRD pattern for Calcined ball clay shows a diminished presence of impurities. This further agrees with literature that calcination reduces impurities from clay.

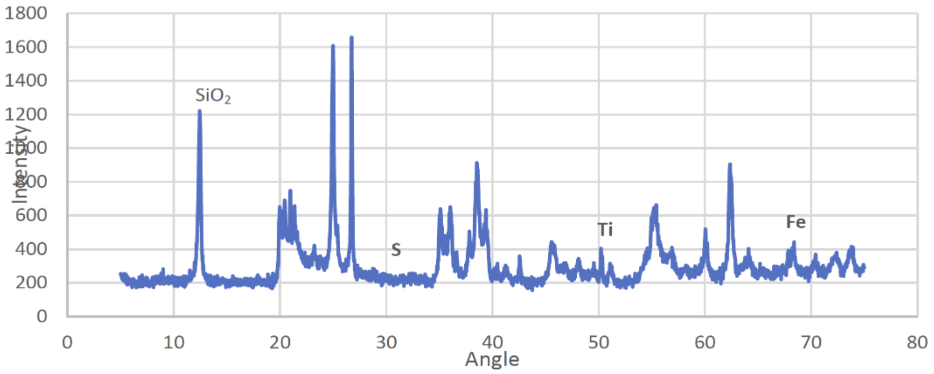


Figure 4.3: XRD Characterization for Raw Ball Clay

Element	Weight Conc. (%)
Si	47.65
Al	30.33
Mg	4.41
Ti	5.02
Fe	4.29

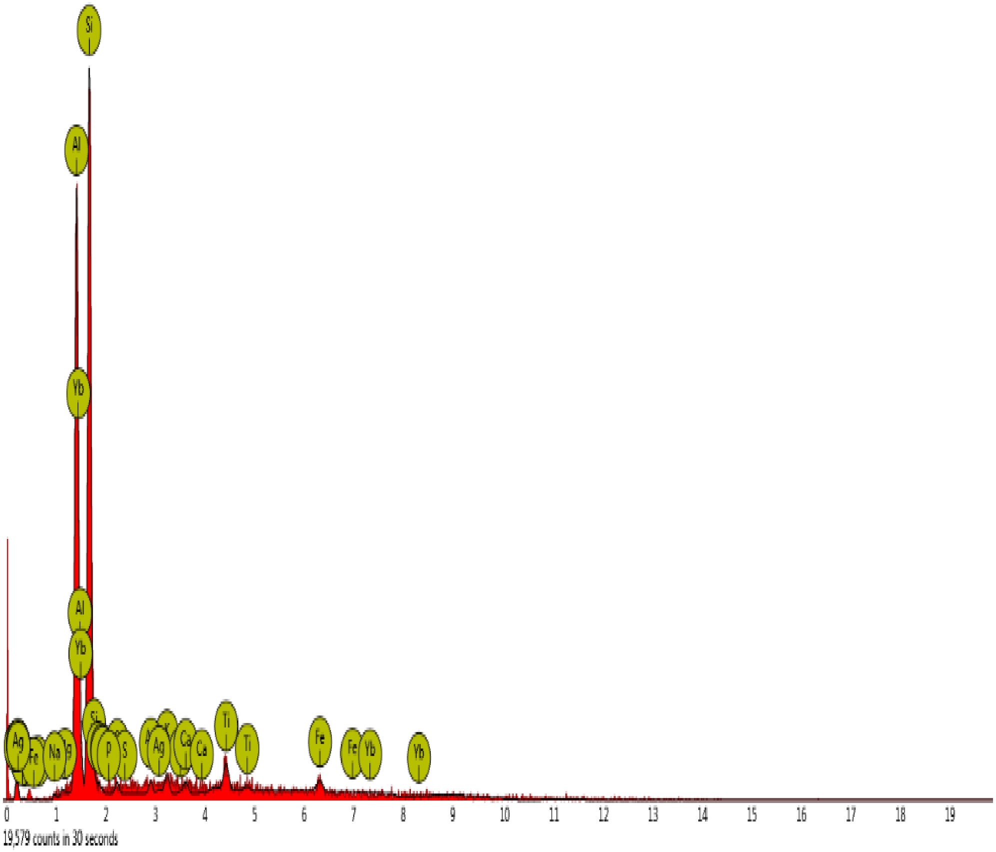


Figure 4.4 EDX Characterization of Raw Ball Clay

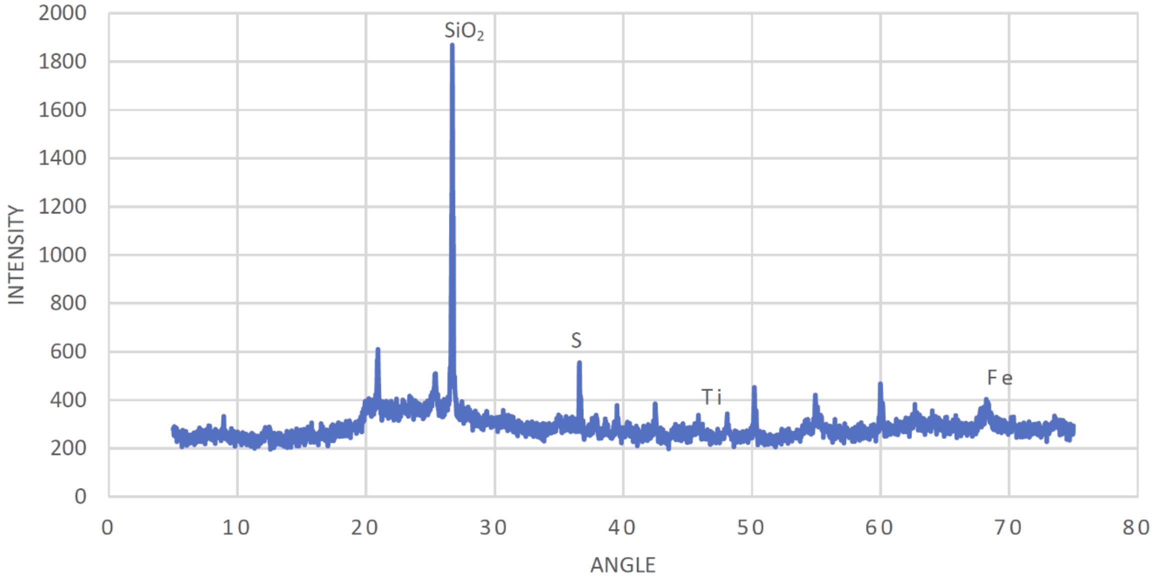
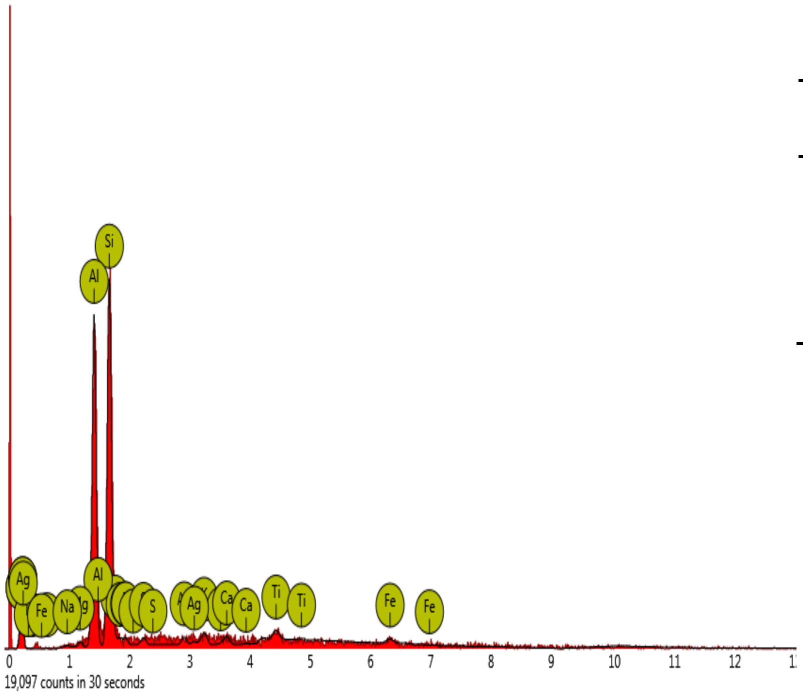


Figure 4.5: XRD Image for Calcined Ball Clay



Element	Weight Conc. (%)
Si	45.79
Al	30.56
Mg	5.05
Ti	3.14
Fe	3.34

Figure 4.6: EDXCharacterization of Calcined Ball Clay

4.3 Impact Strength

The difference in impact strength of HDPE at altered weight fraction of raw and calcined ball clay is shown in Fig. 4.7. The plot shows that impact strength of HDPE-raw and calcined ball clay composite increases with increase in weight fractions. This because there is a very good adhesion between the HDPE and the raw/calcined ball clay, this also has a direct relation to the amount of filler. From the plot, it can be deduced that the impact strength of HDPE and calcined ball clay composite is higher than that of HDPE and raw ball clay composite. Since the structure of free ball clay is not symmetrical, the crystal layers are polarized, which facilitates the ball clay to absorb water molecules (which are also polar) intercalating between the layers. During calcination the absorbed water molecules are diffused out with the concomitant enhancement of molecular randomness that leads to the formation a stable crystalline structure.

From the plot, it can be deduced that at 25% weight fraction the impact strength of HDPE and calcined ball clay composite begin to decline. This is to say that at this ratio the composite with the best impact strength can be obtained while at 30% weight fraction the impact strength peaked for HDPE and raw ball clay.

TABLE 4.1 Impact Strength Test Result for HDPE – Raw and Calcined Ball Clay Composite at various weight fractions.

Impact Strength (J/m)	Calcined Ball Clay	70	86.6	94.3	98.6	115.3	119.5	108.6
	Raw Ball Clay	70	71.8	79.2	80.9	85.1	86.8	99.0
% Weight Fraction		0	5	10	15	20	25	30

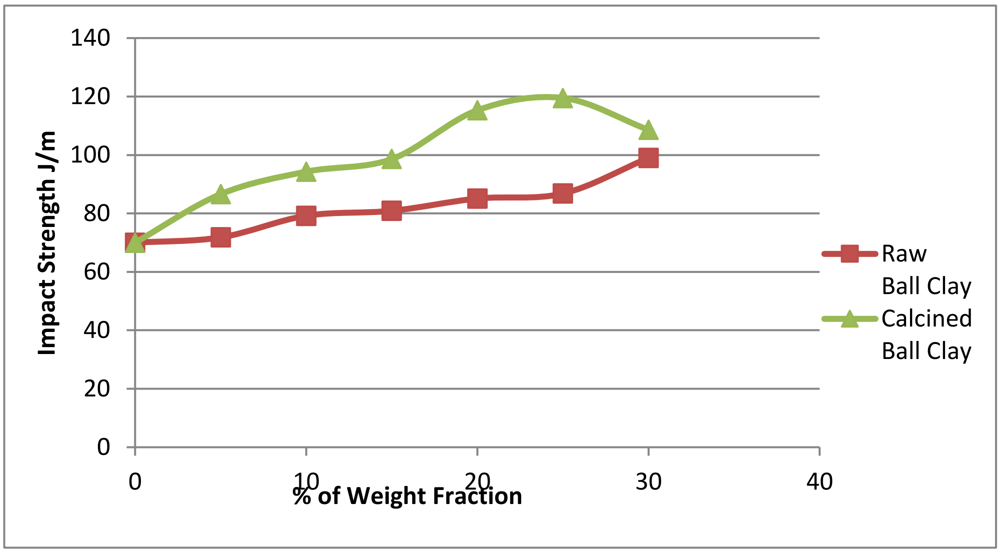


Figure 4.7:Impact Strength of HDPE-Raw and Calcined Ball Clay Composite

4.4 Tensile Strength at Yield

From Figure 4.8, It can be deduced that the variation of tensile strength at yield of HDPE-raw and calcined ball clay composite increases with increasing weight fraction of ball clay. HDPE has less branching, so its intermolecular forces are strong with high tensile strength; whenever it is dispersed with matrix either raw or calcined ball clay. The tensile strength increases with increase in filler content. From this graph, it is quite obvious that the tensile strength of HDPE-Calcined ball clay composite is higher than that of HDPE-Raw ball clay. This difference is obviously owing to the variation in composition and structure of the said ball clay. The polymer composites that contain the calcined ball clay having a high mullite content have improved mechanical properties compared to a similar polymer that does not contain. The relation between the tensile strengths at yield of HDPE at different weight percent of raw and calcined ball clay filler as shown in Figure 4.8 shows that the tensile strength at break of HDPE-Calcined ball clay composite is higher than that of HDPE and Raw ball clay composite. This is quite obvious from the fact that calcined ball clay is not only more rigid and harder than the raw one but also the same can withstand the external stress more efficiently than the raw ball clay composite.

TABLE 4.2 Tensile Strength at Yield Test Result for HDPE – Raw and Calcined Ball Clay Composite at various weight fractions.

Tensile Strength (MPa)	Calcined Ball Clay	29	36.2	41.9	53.2	56.3	61.8	68.9
	Raw Ball Clay	29	32.1	38.4	45.3	51.4	52.9	48.1
% Weight Fraction		0	5	10	15	20	25	30

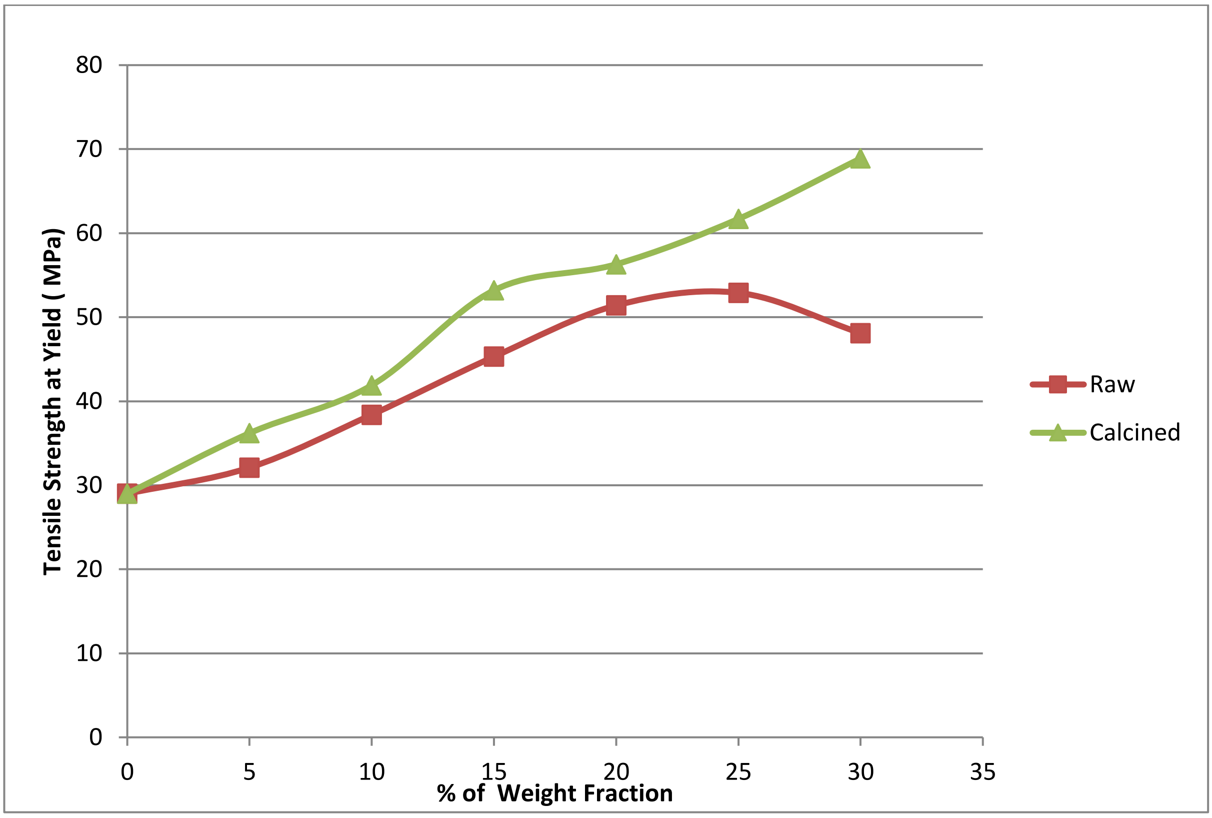


Figure 4.8: Tensile Strength at Yield of HDPE-Raw and HDPE- Calcined Ball Clay Composite

4.5 Thermogravimetric analysis

The results for Thermogravimetric analysis curves for pure HDPE, HDPE-calcined ball clay (CBC) composite and HDPE-raw ball clay (RBC) composite are given in Figure 4.9 and 4.10 for the temperature range 0-600 °C. As evident in the TGA peaks, there are some weight losses observed in the samples. From Figure 4.9, it can be deduced weight loss in sample 100HDPE begins at 360 °C while weight lose begin for 95HDPE/5CBC, 85HDPE/15CBC and 70HDPE/30CBC at 430°C. This indicate that calcination of ball clay improves the TGA of the matrix material. From Figure 4.10, Weight loss for various weight fraction of HDPE-RBC begin around 150°C. This show that calcination of ball clay improves the TGA of HDPE-Ball clay composite.

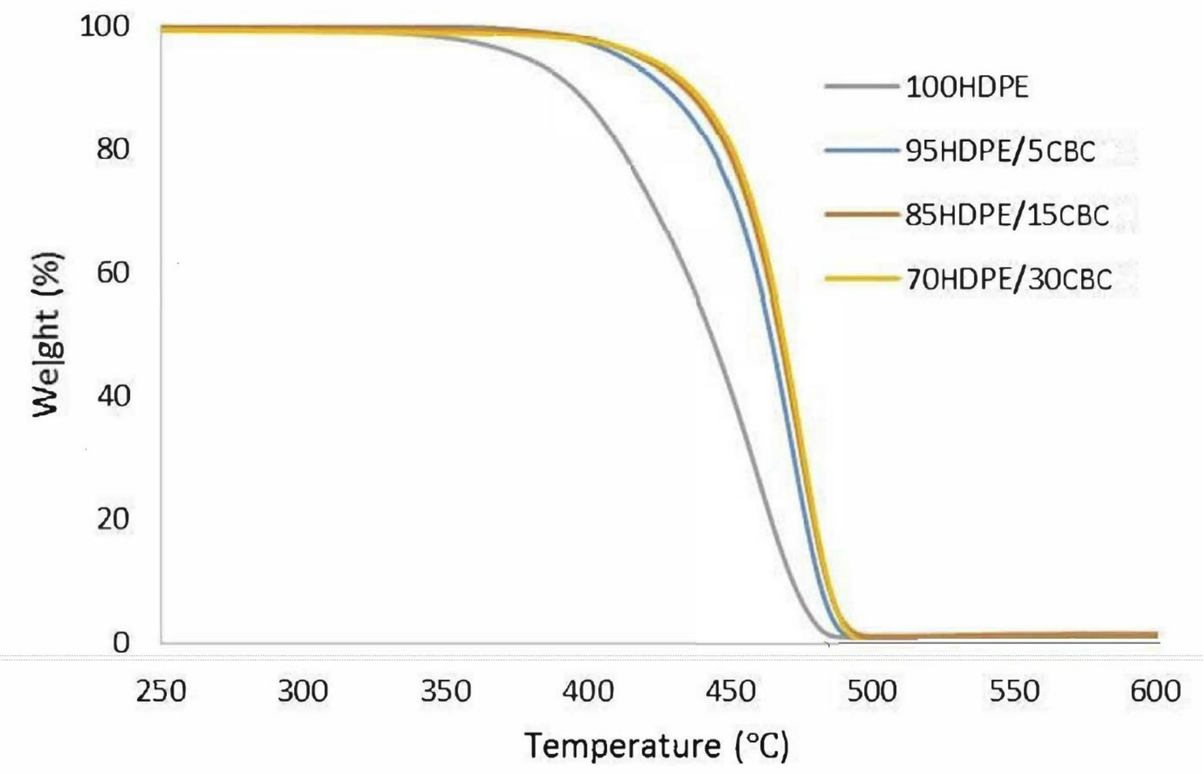


Figure 4.9: TGA Curve Of Pure HDPE And HDPE-CBC Composite

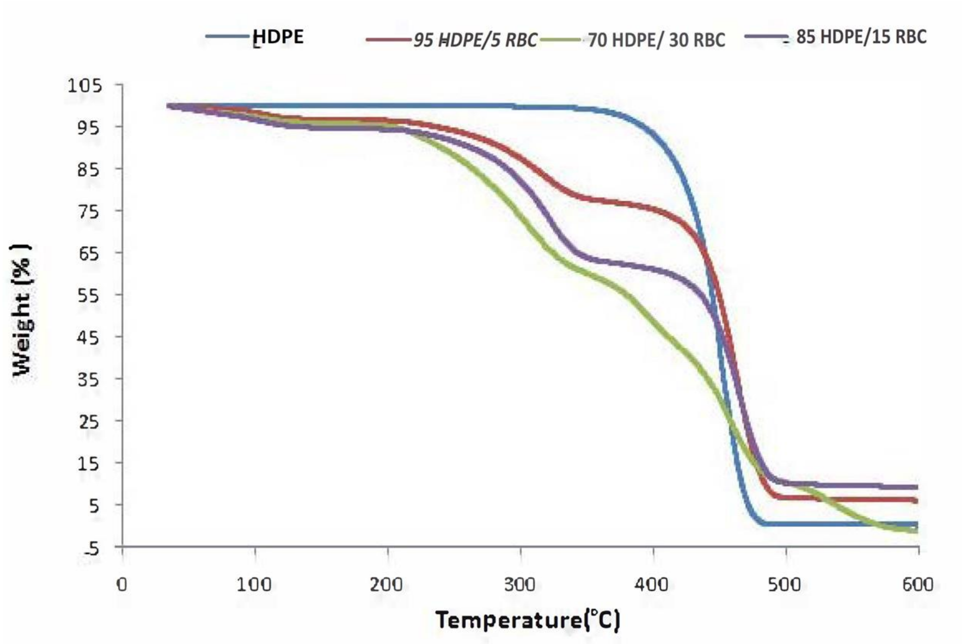


Figure 4.10 : TGA curve of pure HDPE and HDPE-RBC composite

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The use of ball clay as reinforcement in HDPE brings about improvement in mechanical properties. The effect of this filler on the mechanical characteristics of the resulted composites studied shows the difference in Impact strength, and Tensile Strength at Yield value. The impact strength increases as the weight percent of the filler increases both for HDPE-Raw Ball Clay Composite and HDPE-Calcined Ball Clay composite.

It is clear that raw ball clay and calcined ball clay can change the properties of high density polyethylene based on its nature and morphology. It can also be deduced that at 25% weight fraction the impact strength of HDPE-Calcined ball clay composite begin to decline. This is to say that at this ratio the composite with the best impact strength can be obtained while at 30% weight fraction the impact strength peaked for HDPE/raw ball clay.

The results for Thermogravimetric analysis (TGA) curves for pure HDPE, HDPE-calcined ball clay (CBC) composite and HDPE-raw ball clay (RBC) composite for the temperature range 0-600 °C shows some weight losses. It was deduced that weight loss in sample 100HDPE begins at 360 °C while weight lose begin for 95HDPE/5CBC, 85HDPE/15CBC and 70HDPE/30CBC at 430 °C. This indicate that calcination of ball clay improves the TGA of the matrix material. Weight loss for various weight fraction of HDPE-RBC begin around 150°C. This show that calcination of ball clay improves the TGA of HDPE-Ball clay composite.

It is found that the tensile strength at break of HDPE-Calcined ball clay composite is higher than that of HDPE-Raw ball clay composite. This is quite obvious from the fact that calcined ball clay is not only more rigid and harder than the raw one but also the same can withstand the external stress more efficiently than the raw ball clay composite.

5.2 Recommendations

Efforts should be made on similar research more so as to test other physical, mechanical, thermal and electric properties, such as Hardness, thermal coefficient of expansion, resistance to chemicals, electrical resistivity, Dielectric constant, Dielectric strength, thermal conductivity, modulus of elasticity and moisture absorption as there is high possibility that it can be used to manufacture other engineering material.

Automobile industries are also encouraged to embark on more meaningful research work in ensuring the use of HDPE-Raw/Calcined Ball Clay composite products to replace metallic parts. I recommend the results of this research to indigenous car manufacturing companies.

5.3 Contribution to Knowledge

This research has demonstrated that composites formed with 70% HDPE and 30% calcined ball clay and 75% HDPE and 25% raw ball clay gives the optimum tensile strength of 120 j/m and 100 j/m respectively. It further demonstrated that optimum impact strength of 70 MPa and 53 MPa is achieved at 75% HDPE and 25% calcined ball clay and 70% HDPE and 30% raw ball clay respectively. Furthermore, weight loss of 100% HDPE begins at 360°C while weight lose begin for 95 % HDPE and 5% calcined ball clay, 85% HDPE and 15% calcined ball clay and 70% HDPE and 30% Calcined ball clay at 430 °C.

REFERENCES

Abdullah, A., Abedin, M., Beg, M., Pickering K., & Khan, M., (2006). Study on the mechanical properties of jute/glass fiber-reinforced unsaturated polyester hybrid composites: effect of surface modification by ultraviolet radiation, *Journal of Reinforced Plastics and Composites*, 25(6), 575–588.

Abilash, N., & Sivapragash, M.,(2011). Assesment of self healing property in hybrid fiber polymeric composite," *International Journal of Engineering Science and Technology (IJEST)*, 3(7) 5430–5435.

Agarwal, A., (2010). Tensile behaviour of glass fiber reinforced plastics subjected to different environmental conditions, *Indian Journal of Engineering and Materials Sciences*, (6) 471–476.

Ahmed, K., & Vijayarangan, S., (2008). Tensile, flexural and interlaminar shear properties of woven jute and jute-glass fabric reinforced polyester composites. *Journal ofMaterials Processing Technology*, 207 (1–3) 330–335.

Ahmed, K., Vijayarangan, S., & Naidu, A., (2007). Elastic properties, notched strength and fracture criterion in untreated woven jute-glass fabric reinforced polyester hybrid composites. *Materials and Design* 28 (8) 2287–2294.

Ahmed, K., S. Vijayarangan, & Rajput, C., (2006). Mechanical behavior of isothalic polyester-based untreated woven jute and glass fabric hybrid composites. *Journal of Reinforced Plastics and Composites* 25 (15)1549–1569.

American Chemistry Council, (2014). Plastics and polymer composites technology roadmap for automotive markets, Washington, DC: American Chemistry Council – Plastic Division.

Amit, M., & Anil K., (2015). Comparative studies on physico-mechanical properties of composite materials of low-density polyethylene and raw/calcined kaolin, *Journal of Asian Ceramic Societies*,3(2) 212-216.

Aquino, E., Sarmento, S., Oliveira, W., & Silva, R., (2007). Moisture effect on degradation of jute/glass hybrid composites, *Journal of Reinforced Plastics and Composites*, 26(2), 219–233.

Arens, P., (1951). A study of the differential thermal analysis of clays and clay minerals Excelsiors Foto-offset, Wageningen, Netherlands.

Baioumy, H., & Ismael, S. I. (2014). Composition, origin and industrial suitability of the Aswan ball clays. *Egypt Applied Clay Science,* 102: 202-212.

Bajpai, P., Meena, D., Vatsa, S., & Singh, I., (2013). Tensile behaviour of nettle fiber composites exposed to various environments. Journal of Natural Fibers,10(3), 244-256.

Bardis, J., Kedward, K., Bish, J., & T. K. Tsotsis, (2009). Alternate compression test method for notched and unnotched composites, in *Proceedings of the 45th International SAMPE Symposium and Exhibition*. 1149–1152

Belingardi, G., Beyene, A.T., Koricho, E.G. & Martorana, B. (2015). Alternative lightweight materials and component manufacturing technologies for vehicle frontal bumper beam, Composite Structures, 120 :483–495.

Bouchetou, M., Ildefonse, J., Poirier J., & Danielou P., (2005). Mullite grown from fired andalusite grains: the role of impurities and of the high temperature liquid phase on the kinetcs of mullitization and the consequences on thermal shocks resistance. Ceramics International 31: 999 – 1005.

Chandrasehar, S., & Ramaswamy, S., (2002). Influence of mineral impurities on the properties of kaolin and it's thermally treated products. Applied Clay Science 21: 133-142.

Cicala, G., Cristaldi, G., Recca, G., Ziegmann, G., A. El-Sabbagh, A., & Dickert, M., (2010). Properties and performances of various hybrid glass/natural fibre composites for curved pipes. Materials & Design 30 (7), 2538-2542.

Datsyuk, V., (2020).Thermal properties enhancement of epoxy resins by incorporating polybenzimidazole nanofibers filled with graphene and carbon nanotubes as reinforcing material Polymer Test, 82, Article 106317.

Dover, E., Skuse, D., & Williams, A., (1990). A Laboratory Study of the Effects of variation in Lee Moor works water composition on the beneficiation of kaolinite, Imerys Minerals Ltd.

Drobny, J., (2014). Handbook of Thermoplastic Elastomers, Oxford, UK: Elsevier Science.

Drzal, L., Rynd, J., & Fort, T., (1983). Effects of calcination on the surface properties of kaolinite. Journal of Colloid and Interface Science 93: 126 – 139.

Etcheverry, M., &Barbosa, S., (2012). Glass fiber reinforced polypropylene mechanical properties enhancement by adhesion improvement. Materials, 5(6), 1084–1113.

European Commission. (2011). Commission recommendation of 18 October 2011 on the definition of nanomaterial. Official *Journal of the European Communities,* 696.

Gamiz, E., Melgosa, M., Sanchez-Maranon, M., Martin-Garci, J., & Delgado, R., (2005). Relationships between chemico-mineralogical composition and color properties in selected natural and calcined Spanish kaolins. Applied Clay Science 28: 269-282.

Geyer, R., Jambeck, J., & Law, K., (2017). Production, use, and fate of all plastics ever made. Sci Adv 3(7), e1700782.

Granta Design Limited. (2015) CES EduPack 2015, [Software] Cambridge, Granta Design.

Grim, R., (1968). Clay Mineralogy, 2 edn Mc-Graw-Hill Book Company, New York, USA.

Grose, D., (2004). The enhancement of flash calcined clay by secondary calcination - MSc Dissertation University of Exeter.

GV, A., Reddy, P., Manoj, M., & Bhaskar, P., (2014). Impact analysis of a car bumper using carbon fiber reinforced PEI and S2 glass/epoxy materials by solid works software, *International Journal of Science Engineering and Advance Technology,* 2(10),565–569.

Hirsch, J., (2011). Aluminium in innovative light-weight car design, Materials Transactions, 52(5) 818–824.

Https://sanitaryware.org/article/ball-clay

Http://www.nigeria.gov.ng/index.php/2016-04-06-08-39-54/north-central/niger-state

Idicula, M., Boudenne, A., Umadevi, L., Ibos, L., Candau, Y., & Thomas, S., (2006). Thermophysical properties of natural fibre reinforced polyester composites. *Composites Science and Technology*, 66 (15) 2719–2725.

Insurance Institue for Highway Safety. Safety. (2015) Bumpers. Available at: http://www.iihs.org/iihs/topics/t/bumpers/qanda (Access 7 January 2021).

James, A., & Poucke, J., (2006). Long glass fiber polypropylene technology for automotive applications', in Society of Polymer Engineers' Automotive Composites Conference, Troy, Michigan, September 12-14, 2006, Michigan: Society of Plastic Engineers.

Jeyanthi, S., (2013). An Investigation of the Use of Natural Fiber Reinforced Thermoplastic Composites for the Automotive Bumper Beams, PhD thesis, Anna University, Chennai, India.

John, K., & Venkata, S., (2004). Effect of fiber content and fiber treatment on flexural properties of sisal fiber/glass fiber hybrid composites. *Journal of Reinforced Plastics and Composites*, 23(15) 1601–1605.

John, K., & Venkata, S., (2004). Sisal fiber/glass fiber hybrid composites: the impact and compressive properties. *Journal of Reinforced Plastics and Composites*, 23, (12) 1253–1258.

John, K., & Venkata, S., (2004). Tensile properties of unsaturated polyester-based sisal fiber: glass fiber hybrid composites. *Journal of Reinforced Plastics and Composites* 23 (17) 1815–1819.

Khalil, H., Jawaid, M., & Bakar, A.,(2011). Woven hybrid composites: water absorption and thickness swelling behaviours BioResources, 6, 1043-1052.

Khanam, P., et al., (2010). Sisal/Carbon fibre reinforced hybrid composites: tensile, flexural and chemical resistance properties. *Journal of Polymers and the Environment*, 18(4), 727–733.

Khan, M., Ganster, J., & Fink, H., (2009). Hybrid composites of jute and man-made cellulose fibers with polypropylene by injection moulding. *Composites A*, 40(6- 7) 846–851.

Kumar, N., Reddy, G., Naidu, S., Rani, T., & Subha, M., (2009). Mechanical properties of coir/glass fiber phenolic resin based composites. *Journal of Reinforced Plastics and Composites*, 28(21) 2605–2613.

Miller, L., Soulliere, K., Sawyer-Beaulieu, S., Tseng, S. &Tam, E. (2014) 'Challenges and alternatives to plastics recycling in the automotive sector', Materials, 7(8) 5883–5902.

Mohan, R., Kishore, K., Shridhar, M., & Rao, R.,(1983). Compressive strength of jute-glass hybrid fibre composites. *Journal of Materials Science Letters*, 2(3), 99–102.

Naidu, V., Reddy, G., & Kumar, M.,(2011). Thermal conductivity of Sisal/Glass fibre reinforced hybrid composites. *International Journal of Fiber and Textile Research*,1(1), 28–30.

Nanocor. (2008) Nanoclay Structures. Available at: http://www.nanocor.com/nano_struct.asp (access 7 January 2021).

Nanowerk. (2012) Polymer Nanocomposites Drive Opportunities in the Automotive Sector. Available at: http://www.nanowerk.com/spotlight/spotid=23934.php (access 8 January 2021).

Noble, F., (1980). A study of sintering and other phenomena related to calcination in the Lee Moor No.3 Herreschoff Imerys Minerals Ltd.

Rahmat, M., & Hubert, P., (2011). Carbon nanotube–polymer interactions in nanocomposites: a review', Composites Science and Technology, 72(1), 72–84.

Rozman, H., Hazlan, A., & Abubakar, A., (2004). Preliminary study on mechanical and dimensional stability of rice husk-glass fiber hybrid polyester composites, *Polymer-Plastics Technology and Engineering*, 43(4), 1129–1140.

Schneider, H., Oka, K.,& Pak, J., (1994). Mullite and Mullite Ceramics John Wiley and Sons, Chichester, England,105 - 145.

Srinivasan, M., (2014). Applied Solid State Physics: A Textbook on Material Science, Turnbridge Wells, UK: New Academic Science.

Steel Market Development Institute. (2013) Steel Bumper Systems for Passenger Cars and Light Truck, 5th ed., Michigan: Steel Market Development Institute.

Stewart, D., (2008). Calcined Kaolin in Decorative Matt Emulsions Presentation Imerys Minerals.

Sugden, A., (2003). An introduction to whiteware fluxes Imerys Minerals Ltd.

Suresh, S., & Kumar, V., (2014). Experimental determination of the mechanical behavior of glass fiber reinforced polypropylene composites, Procedia Engineering, Vol. 97,.632–641.

Sutar, V., Dharankar, C., & Raju, B., (2015). High strength steel for automotive applications. International Research Journal of Engineering and Technology, 3(5), 966–968.

Tamrakar, S., & Lopez-Anido, R.,(2011). Water absorption of wood polypropylene composite sheet piles and its influence on mechanical properties. *Construction and Building Materials*, 25(10), 3977–3988.

Taylor, R., (2000). Microwave assisted firing of kaolinite Imerys Minerals Ltd.

Tserpes, K., & Labeas, G.,(2009). Mesomechanical analysis of non-crimp fabric composite structural parts. Composite Structures, 87 (4), 358–369.

Tewari, M., Singh, V., Gope, P., & Chaudhary, A., (2012). Evaluation of mechanical properties of bagasse-glass fiber reinforced composite. *Journal of Materials and Environmental Science,* 3(10) 171–184.

Thrale, D., & Adams, J., (1991). Methods for improving the colour of calcined clays Imerys Minerals Ltd.

Thrale, D., Smith, D., & Williams, A., (1990). The colour of calcined clays Imerys Minerals Ltd.

Thwe, M., & Liao, K., (2002). Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites Science and Technology*, 63(3-4) 375–387.

Thwe, M., & Liao, K., (2002). Effects of environmental aging on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites A*, 33(1), 43–52.

Velmurugan, R., & Manikandan, V., (2007). Mechanical properties of palmyra/glass fiber hybrid composites, *Composites Part A: Applied Science and Manufacturing*, 38(10), 2216–2226.

Vlasova, N., (1988). Influence of the degree of filling and the properties of the fillers on the strain-strength properties of synthetic polyethylene composite. Polym. Sci., 30, 1487–1494.

Van de Werken, N., (2020). Additively manufactured carbon fiber-reinforced composites: state of the art and perspective Additive Manufacturing.

Wan, Y., Gong, L., Tang, L., Wu, L., & Jiang, J., (2014). Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide, Composites Part A: Applied Science and Manufacturing, (64)79–89.

William, D., & D.G. Rethwisch, D., (2007). Fundamentals of Materials Science and Engineering: An Integrated Approach, 3rd ed., John Wiley, New York.

William, D., (2000). Materials Science and Engineering: An Introduction, 5th ed., Wiley, New York.

Worral, W., (1975). Clay and Ceramic Raw Materials, Applied Science Publishers Ltd., London.

Yaakob, W., Azira, W., & A. Ismail, E., (2007). Tensile behaviour of hybrid natural/glass fibers reinforced composites at different temperatures. *Conference on Energy and Environment*, Kuching, Sarawak.

APPENDIX

APPENDIX A: Mass Of High Density Polyethylene (HDPE) And Raw BallClay Composites

Sample	Mass of virgin HDPE used (g)	Mass Raw Ball Clay used(g)	%weight fraction
A_1	1000	0	0
A_2	950	50	5
A_3	900	100	10
A_4	850	150	15
A_5	800	200	20
A_6	750	250	25
A_7	700	300	30

APPENDIX B: Mass of High Density Polyethylene and Calcined Ball Clay Composites

Sample	Mass of virgin HDPE used (g)	Mass Raw Calcined Clay used(g)	% weight fraction of Calcined Ball clay
B_1	1000	0	0
B_2	950	50	5
B_3	900	100	10
B_4	850	150	15
B_5	800	200	20
B_6	750	250	25
B_7	700	300	30

APPENDIX C: Typical Characteristics Of High Density Polyethylene (Source: Indorama Eleme Petrochemicals Technical Data Sheet)

PROPERTY	TEST METHOD	UNIT	VALUE
Melt Flow Index (190^0C/2.16 kg)	ASTM D 1238	gm/10 min.	4.5
Density	ASTM D 792	gm/cm3	0.956
Tensile Strength at Yield	ASTM D 638	MPa	29
Elongation at Break	ASTM D 638	%	850
Flexural Yield Strength	ASTM D 790	MPa	31
Flexural Modulus	ASTM D 790	MPa	900
Impact Strength	ASTM D 256	J/m	70
Vicat Softening Point	ASTM D 1525	^{0}C	128
Hardness	ASTM D 2240	Shore D	69

APPENDIX D: Impact Strength Test Result for HDPE – Raw and Calcined Ball Clay Composite at various weight fractions

Impact Strength (J/m)	Calcined Ball Clay	70	86.6	94.3	98.6	115.3	119.5	108.6
	Raw Ball Clay	70	71.8	79.2	80.9	85.1	86.8	99.0
% Weight Fraction		0	5	10	15	20	25	30

APPENDIX E: Tensile Strength At Yield Test Result For HDPE – Raw And Calcined Ball Clay Composite At Various Weight Fractions

Tensile Strength (MPa)	Calcined Ball Clay	29	36.2	41.9	53.2	56.3	61.8	68.9
	Raw Ball Clay	29	32.1	38.4	45.3	51.4	52.9	48.1
% Weight Fraction		0	5	10	15	20	25	30