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Investigating the Performance of Upvc Pipes with Alumina Derived From Natural Kaolin

Ayitegeb, Birhanu

Wisdom at the source of the Blue Nile

BAHIR DAR UNIVERSITY

BAHIR DAR INSTITUTE OF TECHNOLOGY

SCHOOL OF RESEARCH AND POST GRADUATE STUDIES

FACULTY OF CHEMICAL AND FOOD ENGINEERING

INVESTIGATING THE PERFORMANCE OF UPVC PIPES WITH ALUMINA DERIVED FROM NATURAL KAOLIN

BY

BIRHANU AYITEGEB

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Bahir Dar, Ethiopia

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BIRHANU AYITEGEB AMBAW

A Thesis

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DECLARATION

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Name of the student: Birhanu Ayitegeb   Signature _____

Date of submission: 01/03/2012 E-C

Place: Bahir Dar

This thesis has been submitted for examination with my approval as a university advisor.

Advisor Name: Zenamrkose Bantie (PhD)

Advisor's Signature: _____

Bahir Dar University

Bahir Dar Institute of Technology

School of Research and Graduate Studies

Faculty of Chemical and Food Engineering

APPROVAL SHEET

Student:

Birhanu Ayitegeb / / 03/01/2012 E-C

Name   Signature   Date

The following graduate faculty members certify that this student has successfully presented
the necessary written final thesis and oral presentation for partial fulfillment of the thesis
requirements for the Degree of Master of Science in ProcessEngineering.

Approved by:

Advisor:

Zenamrkose Bantie (PhD) / / 03/01/2012 E-C

Name   Signature   Date

External Examiner:

Betelay Tekola (PhD) / for / 03/01/2012 EC

Name   Signature   Date

Internal Examiner:

Solomon Workneh (PhD) / / 03/0/2012 E-c

Name   Signature   Date

Chair Holder:

Metadel Kasahun (PhD) / / 03.01.2012 EG

Name   Signature   Date

Faculty Dean:

Mr.Ali Sied / / 03-01-2012 EC

Name   Signature   Date

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ABSTRACT

This study was devoted to investigating   the performance of Unplasticized polyvinyl chloride (UPVC) pipe filled with alumina (Al_2O_3) and comparing with calcium carbonate ($CaCO_3$) filler at different weight fractions. In addition to this identifying the optimum condition to extract alumina from kaolin clay was also analyzed. During extraction, the alumina was leached out by considering three factors i.e. concentration of H_2SO_4, time and temperature and the optimum extraction condition was obtained at 5M of H_2SO_4,4hr, and 80 ^{o}c, which provide about 62 % of alumina. An analysis was made to characterize or to confirm that the extracted product was the targeted alumina or not by using analytical methods such as FTIR, XRD, AAB, and TGA. The fillers were incorporated on loading ratio of 20 and 25 % into the matrix of UPVC. These composites (filled pipes) were investigated for their mechanical properties (such as ultimate tensile strength, flexural strength, impact resistance, hardness, as well as hydrostatic pressure test), thermal properties (i.e. Vicat softening, rate of change in the mass of a pipe as a function of temperature), and the. Specific gravity. From the results, it was found that there is significant improvement in mechanical properties such as impact resistance, tensile and flexural strengths with the increment of addition of filler material. When the content of alumina was increased from 20 to 25 %, the ultimate tensile strength also increased from 4.7 Mpa to 5.3Mpa. However, the ultimate tensile strength of the pipe filled with calcium carbonate was decreased from 2.78 Mpa to 1.95 Mpa when the calcium carbonate content was increased from 20 to 25 %. Additionally, the introduction of filler (Al_2O_3 and Ca_2CO_3) into the UPVC matrix results in enhancement in processing and functional properties, especially thermal stability and Vicat softening temperature. Finally, it was found that ,when the contents of alumina increased from 20 % to 25 % ,there were improvement in stiffness (2.25 to 2.32 Mpa),flexural strength (22.7 to 23.7 Mpa) ,impact resistance (3.36 KN/8cm to 4.50 KN/ 8cm) ,hydrostatic bursting time at 35.4 bar(1.43 hr. to 1.88 hr.), Vicat softening (98.30 ^{o}c to 101.11 ^{o}c),and specific gravity (1.47 to 1.5). Similarly when the calcium carbonate content increased from 20 % to 25 %, there were an improvement in stiffness (2.3 to 2.5 Mpa), flexural strength (18.08 to 19.76 Mpa), impact resistance (2.56 KN/8cm to 2.77 KN/8cm), Vicat softening (86.58 ^{o}c to 89.93 ^{o}c), and specific gravity (1.34 to 1.39),however the hydrostatic bursting time at 35.4 bar decreased from 0.18 hr. to 0.12 hr.

Key words: UPVC. Mechanical Properties, Thermal properties, Filler (Alumina)

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ABBREVIATION

AAS	Atomic absorption spectro photometer
APF	Amhara pipe factory
FTIR	Fourier transform infra-red spectroscopy
HDPE	High density poly ethylene
LDPE	Low density poly ethylene
OD	Outside diameter
PP	Poly propylene
PVC	Polyvinyl chloride
TGA	Thermogravimeteric analyzer
UPVC	unplasticized Polyvinyl chloride
XRD	X-ray diffractin

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Polymers have substituted many conventional materials, especially metals, in various applications due to the superior advantages over conventional materials (Wirawan et al., 2009). They are used in all classes of materials from household items to different exterior products because of their versatile properties such as light weight, resistance to breakage, low cost, ease of manufacturing, fabrication, and shaping. Moreover, they can also be used widely with other materials to improve various properties. Amongst the different types of plastics, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and polyvinyl chloride (PVC) are mostly used in industries (Deka *et al*., 2011).

Plastics can be used in many applications, ranging from replacement windows to packaging materials, and from mundane products such as disposable cutlery to highly specialized components in electrical and aerospace products (Yoon and Han, 2000) . With a today's worldwide annual production capacity of approximately more than 30 million tonnes, UPVC is the second largest volume thermoplastic only to polyethylene as volume leader in the plastics industry. Its ability to be compounded with many additives to a wide range of flexible and rigid products constitutes the major factor responsible for the versatile application of UPVC, (e.g. for pipes, profiles, floor coverings, cable insulation, roofing sheets, packaging foils, bottles, and medical products) (Braun, 2002).

Poly vinyl chloride differs from other thermoplastics with regard to the possibility of wide-ranging modification of physicochemical, mechanical and processing properties by applying various processing additives to UPVC blends, including fillers (Klapiszewski *et al*., 2015). Fillers are widely used in thermosets, thermoplastics, and elastomers. Current estimates put the global market for fillers at between 12 and 18 million tonnes per year. Originally, their main function was seen as reducing the cost of the finished product.

However, in recent years it has become more widely recognized that fillers can enhance the processability and mechanical properties of compounds (DeArmitt and Rothon, 2002). The most common pipe materials include concrete, ductile iron, vitrified clay, plastic HDPE and PVC, fiberglass, polymer concrete and steel. The term functional filler is often used to describe materials that provide more than cost reduction. Examples of functional fillers include carbon black and precipitated silica reinforcements in tyre treads, aluminum and magnesium hydroxide flame retardant additives for many polymer types, and calcined clay and wollastonite reinforcement of some thermoplastics (Rothon, 2002).

The selection of particular additive is dependent on the end use of the PVC product like PVC-resin is not plasticized for the use in making rigid products such as water pipe, plumbing fittings, and phonograph records. For use in making piping or structural panels that require high resistance to impact, polyvinyl chloride often is blended with small proportions of rubbery synthetic polymers. The modification of rigid PVC having relatively low toughness is carried out by incorporation of a rubbery phase (Unar *et al*., 2010). A very wide variety of particulate material is used as fillers in polymer applications, ranging from apparently simple clays, chalks, and limestone, to rare earth magnetic powders (Rothon, 2002).

The processing of PVC in the raw form using heat and pressure resulted in severe degradation of the polymer due to luck of fillers (Unar *et al*., 2010). Of the several hundred fillers used, those which find spread use are the various grades of $CaCO_3$, quartz and silica filler, talc and various clay. Kaolinite has been used as a filler for thermoplastics. Kaolinite is characterized by small grain size and plate shape. These properties are useful in the production of a compound with high strength and electrical insulation (Mekhemer *et al*., 2000).

Clay in its pure condition is comparatively rarely found, the larger portion of the deposit being composed of impure clay. Pure clay is a silicate of aluminum and when found in large quantities, it is called kaolin (Sol-Gel, 2005). All other clays contain various impurities (other minerals) and it is these impurities that give the clays their particular characteristics and colors. Silica is the dominant constituent of clays, with alumina being essential as well (Thabet *et al*., 2011). The clay minerals in such high-alumina

clays commonly are in the kaolin group and the clay rocks (mixtures) that contain Al_2O_3 in excess (Keller, 1964). Kaolin is a significant raw material with widespread application in the industrial area including water treatment, as porcelain, cement, and ceramics production and equally useful as fillers for polymer, paint and rubber.

Kaolin, or china clay, nevertheless relatively rare in nature, is of specific importance to the potter (Yahaya *et al*., 2017). The fact that the clay substance with many of its impurities is cleaned by sulfuric acid which enables the separation of the clay substance from the sand or quartz (Weems, 1904). Kaolin contains 20 - 26 percent by weight of alumina. Therefore, it can be a suitable material for production or synthesis of alumina because of its abundance and have considerable content of alumina in kaolin structure (Aliyu *et al*., 2016). Alumina (Al_2O_3) is widely used as filler material because of its ability to make the composite with high elastic modulus, high wear resistance, chemical corrosion resistance, stability, and retention of strength at high temperatures. However, higher brittleness and accumulation of particles during the fabrication process cause limitations in its usage (Mohanty *et al*., 2014)

APF is the largest among the very few factories that produce plastic products in Ethiopia. The factory has produced and supplied different ranges of pipes (PVC and HDPE) and Geomembrane sheet with encouraging performance. Since its establishment is by considering irrigation and water supply for the region in particular and the nation in general, thus the factory pays high attentions how to enhance the quality of PVC pipe (strength). The factory plans to become "Technology Transfer Company" and center of skill transfer for many professionals and researchers to alleviate the limitations and weaknesses observed on the quality of the products (Degu, 2014).

1.2. Statement of problem

Pure UPVC is a polymer at room temperature with low thermal stability. Hence, UPVC requires heat stabilizers during processing at high temperatures addition of filler is necessary (Elias, 1984). The use large amounts of filler without impairing the quality of the UPVC has a great commercial advantage on the cost of the finished product due to the low cost of filler than UPVC.

The filler commonly used (calcium carbonate) has its own disadvantages. For example, if the amount is greater than 20 parts per hundred parts of resin., the acid resistance and brittleness of the finished product would be unacceptable.   In addition to this, due to the solubility properties of calcium carbonate , it is being washed away by moisture and rain, leaving a porous surface layer on UPVC pipe and it is converted to calcium sulfate because of its reaction with sulfur dioxide ,which is a common pollutant(Underwood and Bohm, 1981.

However, alumina can be used as a filler beyond 20 parts per hundred parts of resin, with the increments of performance of pipe (Underwood and Bohm, 1981). In addition to this alumina (aluminum oxide) is insoluble in water and most commonly it's occurring is in crystalline form (Degu, 2014).

The production output of the factory (APF) is mainly affected by the availability of raw material and market. Raw materials including the filler are imported from abroad. The alternative filler that can substitute calcium carbonate like alumina from kaolin is cheap, abundant and readily available in most part of the world including Ethiopia (Kunwar, 2012). While UPVC is a popular material for pipe construction in APF, it has its limitations. UPVC is known to undergo thermal and photo-oxidative degradation. The amorphous structure parameters of UPVC are also influence on the final product quality. Among UPVC pipe defects about 44.4% of defects are contributed by shrinkage. Thickness variations, inner diameter variation are also other contributors of the company's pipe defects. UPVC is prone to fractures due to environmental stress. Basically all the above limitations can be eradicated with the help of filler (alumina) (Deshmukh, 2014).

1.3. Objective of the study

1.3.1. General objective

The principal aim of this research is to investigate the performance of UPVC pipes using alumina from kaolin as filler in comparison with limestone ($CaCO_3$) fillers.

1.3.2. Specific objective

➢ To synthesis and characterize alumina from natural kaolin using different techniques (AAB, FTIR, XRD, TGA,).

➢ To investigate the effect of operating parameters such as H_2SO_4 concentration, temperature and time in alumina extraction.

➢ To evaluate the performance of UPVC pipe produced by using alumina from kaolin as a filler and comparing with commercially available UPVC pipes filled with calcium carbonate.

1.4. The scope of the study

This study was devoted to extract alumina from kaolin and characterize the extracted alumina by using FTIR, XRD, TGA and AAB. Once the alumina was extracted and analyzed the UPVC pipe is produced by using alumina as a filler. Finally, the pipe mechanical, physical and thermal property is characterized and compared with the commercial products of the APF factory, which filled with calcium carbonate.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. "UPVC" Material

UPVC stands for un-plasticized polyvinyl chloride. It is said to be un-plasticized because no additive is added to make the material flexible instead of being rigid. It is a thermoplastic material with high rigidity and high modulus of elasticity. Thanks to modern science and many years of research and development that UPVC has become the most sophisticated substances available for windows, doors, shutters, automobile body parts, building material, and even credit cards (Kunwar, 2012). One of the largest industrial applications of unplasticised polyvinyl chloride (UPVC) is used in pipe systems because it has the following advantages: high impact strength, relatively lower cost, recyclable , beautiful and stylish with standard-sized holes for locks and knobs , wide variety of finishes , energy-saving and heat-reflective, easy to clean , soundproof . Furthermore, unlike wooden or metal doors, windows and frames made from UPVC exhibits the following stand out features: termite resistant, corrosion-free, fire-resistant, moisture resistant, lower maintenance lost. unique profiles (Visser *et al*.).

Vinyl chloride is a monomer which makes up polyvinyl chloride. It was identified by the environmental protection agency and other agencies as carcinogenic. The vinyl chloride can transport itself from the pipe into the water to residential and commercial areas. If the polymer is inhaled for a given period of time, it spreads first to the liver and kidneys and then to the lungs and spleen (Deshmukh, 2014).

2.1.1. Characteristics of UPVC and HDPE

Un plasticized polyvinyl chloride (UPVC) is amorphous, cheap and durable vinyl polymer used in construction projects while high density polyethylene (HDPE) is semi-crystalline a polyethylene thermoplastic that is made from petroleum. Both are strong and durable, but their strengths vary and they have different applications. UPVC is heavier and stronger while HDPE is harder and more abrasion and heat resistant (Peacock, 2000).

HDPE pipes are found to be able to dampen and absorb shock waves minimizing surges that can affect the system while, UPVC cannot. HDPE is a thermoplastic material

composed of carbon and hydrogen atoms joined together forming high molecular weight which converted into ethylene products. 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 atoms, and consequently, the greater the molecular weight. The molecular weight, the molecular weight distribution and the amount of branching determine many of the mechanical and chemical properties of the end product. Characteristics such as tensile yield strength and stiffness (flexural or tensile modulus) are increased as density is increased. (Gabriel, 1998). The composition of UPVC is about 57% of chlorine which is derived from industrial grade salt and about 43% of carbon, mostly taken from oil and gas from ethylene. Therefore, UPVC is less dependent on crude oil or natural gas than the other polymers. Chlorine gives UPVC an excellent fire resistance(Thornton, 2002).

2.2. UPVC pipes

Pipes are used widely in different walks of life. They are mostly utilized as service conduits for transport of natural gas, petroleum, chemicals and many other fluids.   Major innovations since 1950 include introduction of ductile iron and use of un plasticized polyvinyl chloride (UPVC) pipe for sewers. The plastic pipes offer a wide range of benefits over the conventional steel and cast-iron pipes. Plastic pipes offer a tremendous weight advantage over alternative piping materials. Normally, Pipe behavior can be broadly classified as flexible or rigid, depending on how it performs when installed. Flexible pipe can move, or deflect, under loads without structural damage. For flexible pipe, deflection allows loads to be transferred to and carried by the backfill. Flexible pipe takes advantage of its ability to move, or deflect, under loads without structural damage (Student and Student, 2016).

UPVC is known to be fracture resistant, and it's this very quality that makes it impermeable to external stresses. It has the ability to withstand soil force and torsion even in places where pressure exists. The pipes are made from such compounds that they can withstand the harshest strength tests compared to metallic pipes (Deshmukh, 2014) . The processing, physicochemical, mechanical and dielectric properties are influenced by other modifiers used in UPVC blends, including fillers. The addition of particles of zinc, aluminum oxide

and calcium carbonate, as well as carbon nanotubes and montmorillonite (MMT) particles, causes an increase in the glass transition temperature compared with the unfilled polymer (Klapiszewski *et al.*, 2015).

2.3. Performance of UPVC pipe

As a viscoelastic material, UPVC exhibits time-dependent properties under stress. Unfortunately, this time dependency is sometimes interpreted as age dependency. For example, the downward slope of the traditional pipe hoop-stress regression curve is often interpreted as a loss of strength with age. In fact, the downward slope simply reflects the ability of the viscoelastic material to support lower stresses for longer periods than it can support higher stresses (Stahmer and Whittle, 2001).

 Pipe failure can be defined as situations in which a pipe can no longer perform its intended task; for example, the pipe is losing water, even though there is no catastrophic failure. The pipe's operational capacity—that is how much water it carries and at what pressure—also determines its life. Pipe damage reflects upon the entire water main infrastructure because it decreases the efficiency and performance of the system. To better understand pipe damages, researchers classified them into two categories: structural deterioration vs. internal deterioration. Structural deterioration occurs when pipes are no longer resilient and lose their ability to respond to applied stresses. Internal deterioration affects the water quality and hydraulic capacity and in turn affects the structural properties of the pipe (Deshmukh, 2014) .

2.4. Clay

Clay is a rather loose term, which is used to describe a variety of widely occurring hydrous aluminosilicate minerals produced by the weathering of granite. These all have sheet structures with variously arranged layers of alumina and silica, and are found as stacks of these layers. The main clay mineral used in the polymer industry is kaolinite ($Al_2O_3.2SiO_2.2H_2O$), usually known as kaolin or china clay. The specific gravity is 2.6, Mohs hardness scale is between 2.5 - 3 and the refractive index is 1.56 (Chukwu and Ajuamiwe, 2013).

2.5. Groups and types of clay

Clays are generally classified as either primary or secondary according to geologic history. Primary clay also known as kaolin ($Al_2O_3.2SiO_2.2H_2O$) is always found or located at the site of formation as feldspar from which they were formed. They are relatively uncontaminated by other minerals and remain unsorted by particle size. The vast majority of clays are called secondary because they have been transported by weathering action of wind and water from their original site of formation. This process involves the loss of certain mineral particles like alumina (Al_2O_3) and silica (SiO_2) concentration is diminished (Ayadi *et al*., 2013).

The clays are generally divided into three classes:

(1) Porcelain clay, which is approximately pure kaolin. When it calcined, it changes to white or light-cream color'.

(2) Plastic clay, which contains more impurities than the porcelain clay. After calcination converted to a yellow-red color and is used for ordinary earthenware.

(3) Fire clays. -. These clays approach very close to the porcelain clays in composition. However, they contain a larger quantity of iron, more silica as quartz. Some of the highest fire clays are very rich in quartz (Weems, 1904).

2.5.1. Chemistry of clay

The changes which take place in the original rock to produce the clay substance may be shown by the following equation, as the result of the action of water and carbon dioxide upon feldspar.

$2Al_2O_3, 2K_2O, 2SiO_2$ (Feldspar) $+ 4H_2O + 2CO_2 = 2Al_2O_3, 3SiO_2, 4H_2O + K_2CO_3 + 9SiO_2$

Kaolin clay substance contains: silica (45.6%), alumina (38.1%), ferric oxide (0.9%), water (13.3%), magnesia (0.7%) etc. Clay, according to Blair, is a mixture of silica and the silicates of aluminum, calcium, magnesium, potassium and sodium. The silicates are hydrated and as a result they may contain from 6 to 12 per cent of water chemically combined. In addition to the substances named, clay may contain ferric oxide, titanic acid, ferric sulfate, organic matter and phosphoric acid. Occasionally, rare elements are found (Weems, 1904).

2.5.2. Kaolinite /Kaolin/China clay

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$. Kaolin particle has two different faces, one with surface oxygens linked to silicon and the other surface hydroxyls linked to aluminum. These particles can stack together into by hydrogen bonding between these two faces. It is layered silicate mineral with one tetrahedral sheet of silica (SiO_2) linked through oxygen atoms to one octahedral sheet of alumina (Al_2O_3) octahedral (Rothon, 2002). Kaolinite can be considered to be almost strictly aluminum-silicates, i.e., no ions other than Al, Si, O, H are present in appreciable quantities in these minerals. These minerals are formed in soils, most noticeably from argillic pelitic and granitic rocks but they are also commonly found forming from basic rocks during the weathering processes (Velde, 2000). This hydrogen bonding is significantly stronger than the van der Waals forces between layers in talc and thus kaolin is a harder mineral.

Rocks that are rich in kaolinite are known as kaolin. The name kaolin was derived from a hill in China (Kao-ling) where it was mined for centuries and which has a soft, light weight, often chalk-like sedimentary rock, earthy odor with plate-like crystal morphology(Cheng *et al*., 2015).

Kaolin is a significant raw material with widespread application in industrial area including water treatment, as porcelain, cement, ceramics production, in the manufacturing of paper, inks, and pains, and equally use as fillers for polymer, paint and rubber. It is also commonly used for the production of clay-based nanocomposites that exhibit unexpected hybrid properties such as enhanced mechanical, thermal, dimensional and barrier performance properties, and flame retardant characteristics (Yahaya *et al*., 2017).

Kaolinite is the main constituent of filler clays, significant quantities of other minerals can often be present, particularly in the cheaper grades. The particle shape is the most important characteristic of kaolinite for polymer applications. The platy nature means that clay fillers have a greater effect on properties such as viscosity, stiffness, and strength than do more isotropic fillers like calcium carbonate(Liew *et al*., 2011).

For some applications, the kaolin is converted into special forms by heating. The main types of converted kaolin for the polymer industry are metakaolin and calcined kaolin

(Ombaka, 2016). Intermediate temperatures lead to the metakaolin (600-800) ^{o}c, which is more chemically reactive than the starting material. Metakaolin has an especially beneficial effect on the electrical resistivity of plasticised UPVC and is mainly used in UPVC cable insulation formulations. Fully calcined kaolin (900-1200) ^{o}c is very inert and used in a variety of polymer applications(Velde, 2000)**.**

2.5.3. The Chemical Composition and structure of Kaolin

The ideal composition for the kaolinites (Al_4 (Si_4O_{10}) (OH) $_8$) is (46.54%) SiO_2, (39.5%) Al_2O_3, and (13.96%) H_2O. However, in nature, this exact composition is seldom, if ever, found. Fe_2O_3, TiO_2, MgO, and CaO are nearly always present in kaolinite samples and K_2O and Na_2O are usually present. Most samples either have excess SiO_2 or Al_2O_3. Mineral impurities such as quartz, anatase, rutile, pyrite, limonite, feldspar, mica, montmorillonite, are commonly present in addition to a number of other minerals (Weems, 1904).

The properties that determine the composition of a mineral are derived from its chemical foundation, the geometric arrangement of atoms and ions, and the electrical forces that bind them together (Yahaya *et al*., 2017). The 1:1 (tetrahedral silica: octahederal alumina) layer minerals contain one tetrahedral and one octahedral sheet in their basic structural unit (Fig. 2.) This two-sheet mineral type is represented by the kaolin group, with the general formula $Al_2Si_2O_5$ (OH)$_4$. Kaolinite, the most common mineral in this group, is dioctahedral, exhibiting Al^{3+} octahedral and Si^{4+} tetrahedral coordination. The sheets are held together by van der Waals bonds between the basal oxygen's of the tetrahedral sheet and the hydroxyls of the octahedral sheet. Layers are held together tightly by hydrogen bonding, which restricts expansion and limits the reactive area to external surfaces (Varga, 2007). Octahedral and tetrahedral are commonly represented using different types of models, each of which portrays the same concept but highlights different structural features (Schulze, 2005).
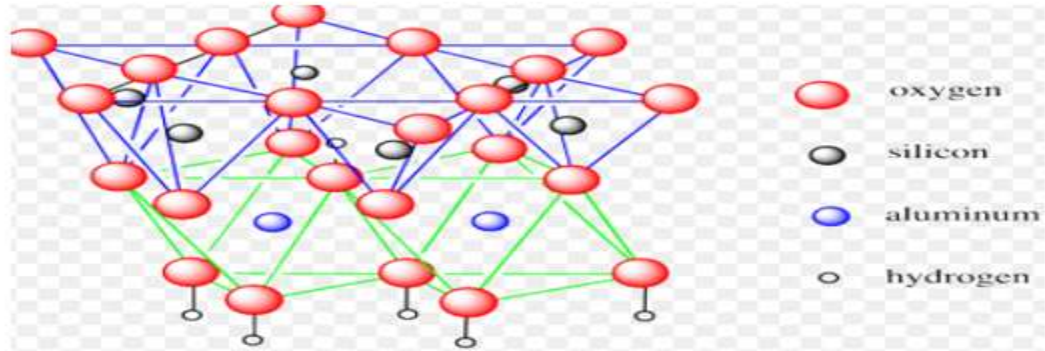
Figure 2. 1 structure of kaolin

2.5.4. Kaolin deposit in Ethiopia

Ethiopia is endowed with a wide variety of minerals and rocks, some of which are available in large quantities and are of excellent quality. Minerals such as potash, bentonite, kyanite, diatomite, graphite, kaolin, marble, granite, limestone, gypsum, sand, etc. occur in sufficiently large reserves that could warrant medium to large-scale mining. Economic kaolin resources of Ethiopia are mostly associated with acidic intrusive rocks (granites and pegmatites) and gneissic rocks. Kaolins hosted by sedimentary rocks are reported in Blue Nile river basin, Ogaden basin and Mekele Outlie (Cannon, 2009). These and the other kaolins which have been investigated in the different parts of the country are summarized in Table 2 and Figure 2.3 (Regassa, 2016).

Table 2. 1 Kaolin occurrence in different parts of Ethiopian

Place	Longitude	Latitude	Region
Belesa	37º 58' E	7 º35' N	SPNNRS
Awzet	38º 07'48" E	11º 45' N	Amhara
DEber Tabor	38º 00' 36" E	11º 50' 02" N	Amhara
Gypsite Mariyam	37º 35' 24" E	11º 45' 36" N	Amhara
Kerker	37º 24' 43" E	12º 42' 40" N	Amhara
Bomboha	38º 46' 30" E	06º05' 20" N	Oromia
Kombeolcha	42º 08' 50" E	09º 27' 58" N	Oromia
Ansho	37º 38'28" E	7º20' 6"N	SPNNRS
Adwa	38º 57' 44" E	14º 19' 54" N	Tigrai
Tsada midri	38º 12' 55" E	14º 26' 42" N	Tigria

Figure 2. 2 kaolin distribution in Ethiopia (Regassa, 2016).

Figure 2. 3 DebreTabor's Kaolin Outcrop (Wondafrash, 2011)

2.6. Additives

The additives used in UPVC formulations are mainly plasticisers, stabilizers, lubricants, and fillers. Plastic additives are foreign substances or materials added to enhance the properties and performance of plastics for specific applications. Before the discovery of additives early plastics were usually unsatisfactory due to the lack of desirable characteristics like shapes, durability and poor processing among others. Plastic additives are now essential in plastic molding even though they cost money in the short term and incorporating them into plastics can be an additional expense. However, they reduce overall production cost and make products last longer (Okpala, 2015).

Some additives can migrate to the surface during use, where they are lost by volatilization or diffusion upon contact with other surfaces. Stabilizers for UPVC have low mobility but

can change their function by consumption or degradation. Fillers usually remain in their initial form and quantity. Thus, to determine if a used UPVC product can be reprocessed, an essential step before reprocessing is the determination of the degree of deterioration of the chemical structure of the base polymer as well as the loss of additives and their functionality (Brown, 2001). The amount of additive used in the formulation varies with respect to the processing technique used in the manufacture of products. Additives are usually employed in small quantities to improve the processing, performance, appearance, and use (Brown, 2001). Metal salts commonly used in UPVC formulations include those of calcium, magnesium, cadmium, zinc, and tin. These may be present either as metal soaps or as stabilizers (Sawyer, 1967)**.**

2.6.1. Filler

Fillers are inorganic particles added to thermoplastic polymers to increase their Young's modulus, improve thermal stability, cost reduction, density control, improved mechanical properties, and reduce wear under friction. Fillers, however, lead to a reduction in the fracture of polymers by embrittlement (Rothon, 2002). In filled polymers, many modes of deformation are distinguishable, for instance, brittleness, quasi-brittle fracture during neck formation, and fracture during neck propagation, stable neck propagation, micro-uniform yielding and yielding in crazes. In filled polymers, crazes are caused by debonding of particles and by stretching of polymers in the space between the neigh-boring particles(Okpala, 2015).

Fillers that are used to replace resin are generally calcium carbonate (limestone), diatomaceous earth, and clays (Braun, 2002).The main fillers in use are: carbon black, precipitated silica, clays, natural calcium carbonate, precipitated calcium carbonate. Approximately 80% of all the filler used in UPVC is calcium carbonate. Titanium dioxide is second at around 12%, followed by calcined clay at about 5%. The remaining few percent others(Hounsham and Titow, 1984).

2.6.1.1. Calcium carbonate

Calcium carbonate is one of the principal mineral fillers used in polymer applications, with the world consumption being over ten million tonnes annually. It is an abundant natural material; with ideal properties for use as a filler in all types of polymer. It occurs in large,

relatively pure, deposits, close to the surface and easily mined. It is nontoxic, with good color, and also relatively soft and easily milled those properties make calcium carbonate as the principal fillers (Tanaka, 2004). There are three different crystal modifications of calcium carbonate, as well as an amorphous form. The crystalline forms are calcite, aragonite, and vaterite, with calcite being the most commonly used form for filler applications. The specific gravity of pure calcite is 2.7 and it has a Mohs hardness of three. At high levels of filler addition normally used where reduction in cost is the primary target, key physical properties like tensile strength, impact Strength, hoop stress are adversely affected. UPVC can only accept lower calcium carbonate filler loadings typically (2–10) (Cheng, 2015).

2.6.2. Alumina /Aluminum oxide

Alumina occurs in clays in the form of clay minerals, in feldspar, mica, hornblende, tourmaline, other alumina-silicates all of which are moderately fusible. Free alumina is also found in some clay derived from bauxites and laterites. Hallosite clays contain associated free alumina in the form of gibbsite (Al (OH) $_3$) making such clays highly refractory because of the high total alumina content. Other clays may contain free alumina as gibbsite, diaspora (AlO.OH) or as a colloidal variety. Aluminous other than clay minerals have the following effect on clays in which they occur: they reduce the plasticity of clay as they are non-plastic, and they increase the refractoriness of clay, provided that the total proportion of alumina is greater than 5%. The refractoriness of a silica brick is drastically reduced by alumina alkalis and other fluxes are usually associated with alumina compounds and these usually have a serious influence in the refractory properties (Dalen *et al*., 2014).

2.6.2.1. Alumina Extraction

Thermal activation followed by selective leaching is performed for the preparation of the porous alumina/silica materials. The leaching of alumina is carried out by using Sulfuric acid with boiling temperature and alkaline concentration. It has been reported that a temperature of 105°C as a recommended extraction temperature, others recommend a temperature of 70–90 °C for 10–12 hours to extract 70–80 % of alumina (Al-Zahrani and Al Zaitone). The surface area, porous structure, and acidity of the kaolin can be improved after acid leaching. Furthermore, acid treatments can replace exchangeable cations with

H^+ ions and Al^{3+} in tetrahedral and octahedral sites, resulting in the improvement of adsorption capacities (Luo *et al*., 2017).

CHAPTER THREE

3. MATERIAL AND METHODS

3.1. Experimental site

This study was carried out in different laboratories mainly in Bahir Dar institute of technology (faculty of chemical and food engineering and mechanical engineering laboratories), Geological survey of Ethiopia, Addis Ababa university of chemistry department (Arat killo), Ethiopian leather industry development institute (LIDI) (Addis Ababa), Amhara pipe factory (Bahir Dar).

3.2. Materials and Chemicals

Kaolin was collected from Debre-Tabor, South Gondar, Ethiopia for the source of alumina which was used as a filler for UPVC pipes production. UPVC resin, CaCO3 filler, lead compound heat stabilizer, titanium die oxide and carbon black were obtained from Amhara pipe factory. Various chemicals were used during this research to accomplish the effective leaching out of alumina from kaolin. Sulfuric acid (98%) was used to completely split metakaolin into its silica and alumina components at different extraction temperatures. Anhydrous sodium hydroxide (NaOH) was used to neutralize leach liquor for enhancing of alumina precipitation. Since positive ion of aluminum is highly attracted by alcohol 97% ethanol was used as precipitating agent. Distilled water was used for the preparation of different solution and washing of kaolin. For the manufacturing of the pipe the following chemicals were also used like UPVC (polyvinyl chloride) resin, $CaCO_3$ filler, alumina filler, lead compound heat stabilizer, titanium die oxide and carbon black.

3.3. Equipments

Table 3. 2 Type of equipments / instruments used

S.N.	Equipment /instrument	Function
1	Water jar	to wash the raw kaolin
2	Oven dryer (PH-030A)	to dry the pretreated kaolin
3	Electric furnace (B130, Germany)	For calcination
4	Water bath (Modee103141504G, England)	For supplying constant leaching temperature
5	FT-IR	To analyze functional groups
6	Universal tensile test machine	For Tensile and flexural measurement
7	Impact measuring machine	To measure Impact resistance
8	Hardness test machine	To Measure Hardness
9	XRD (700 SHIMADZU)	To show crystallinity/amorphous
10	AAB	To quantify elemental compositin
11	TGA	To analyze thermal stability
12	Hydrostatic pressure test machine	To Measure Pressure test
13	Vacat softening machine	To analyze thermal stability
15	Digital balance	For measuring weight of Sample
16	Specific gravity measuring machine	For measuring Relative density
17	Sieves	For separation based particle size
18	Mortar grinder /wooden mortar and pestle	For grinding of sample
19	PH Meter	For PH measurement

3.4. Alumina extraction processes

```
┌──────────┐     ┌──────────┐     ┌──────────────────┐     ┌──────────────────┐
│ Raw      │ ──▶ │ Grinding │ ──▶ │ Mixing and       │ ◀── │ Distilled water  │
│ kaolin   │     │          │     │ settling for 24hr│     │                  │
└──────────┘     └──────────┘     └──────────────────┘     └──────────────────┘
                                            │
                                            ▼
                              ┌──────────────────┐     ┌──────────────┐
                              │   Decantation    │ ──▶ │  Impuritie   │
                              └──────────────────┘     └──────────────┘
                                            │
                                            ▼
                              ┌─────────────────────────┐
                              │ Drying for 24 hr at 60°c │
                              └─────────────────────────┘
                                            │
                                            ▼
                              ┌─────────────────────────┐
                              │        Grinding         │
                              └─────────────────────────┘
                                            │
                                            ▼
                              ┌─────────────────────────┐
          ┌──────────┐        │  Calcination /800 °C for│
          │  H₂SO₄   │ ──────▶│                         │
          └──────────┘        └─────────────────────────┘
                                            │
                                            ▼
                              ┌─────────────────────────┐
                              │ Leaching alumina in      │
                              │      water bath          │
                              └─────────────────────────┘
                                            │
                                            ▼
                              ┌─────────────┐     ┌──────────────────┐
                              │ Filtration  │ ──▶ │  Residue/silica  │
                              └─────────────┘     └──────────────────┘
                                            │
          ┌──────────┐        │        ┌──────────────────────────┐
          │ Ethanol  │ ──────▶│◀────── │ NaOH (for adjusting PH)  │
          └──────────┘        │        └──────────────────────────┘
                                            ▼
                              ┌──────────────────────────┐     ┌──────────────┐
                              │ Precipitation            │ ──▶ │ Supernatant  │
                              │ /sedimentation           │     │              │
                              └──────────────────────────┘     └──────────────┘
                                            │
                                            ▼
                              ┌──────────────────────────┐
                              │ Furnace/1000 °C for 1 hr │
                              └──────────────────────────┘
                                            │
                                            ▼
                              ┌──────────────────────────┐
                              │  Alumina /final product  │
                              └──────────────────────────┘
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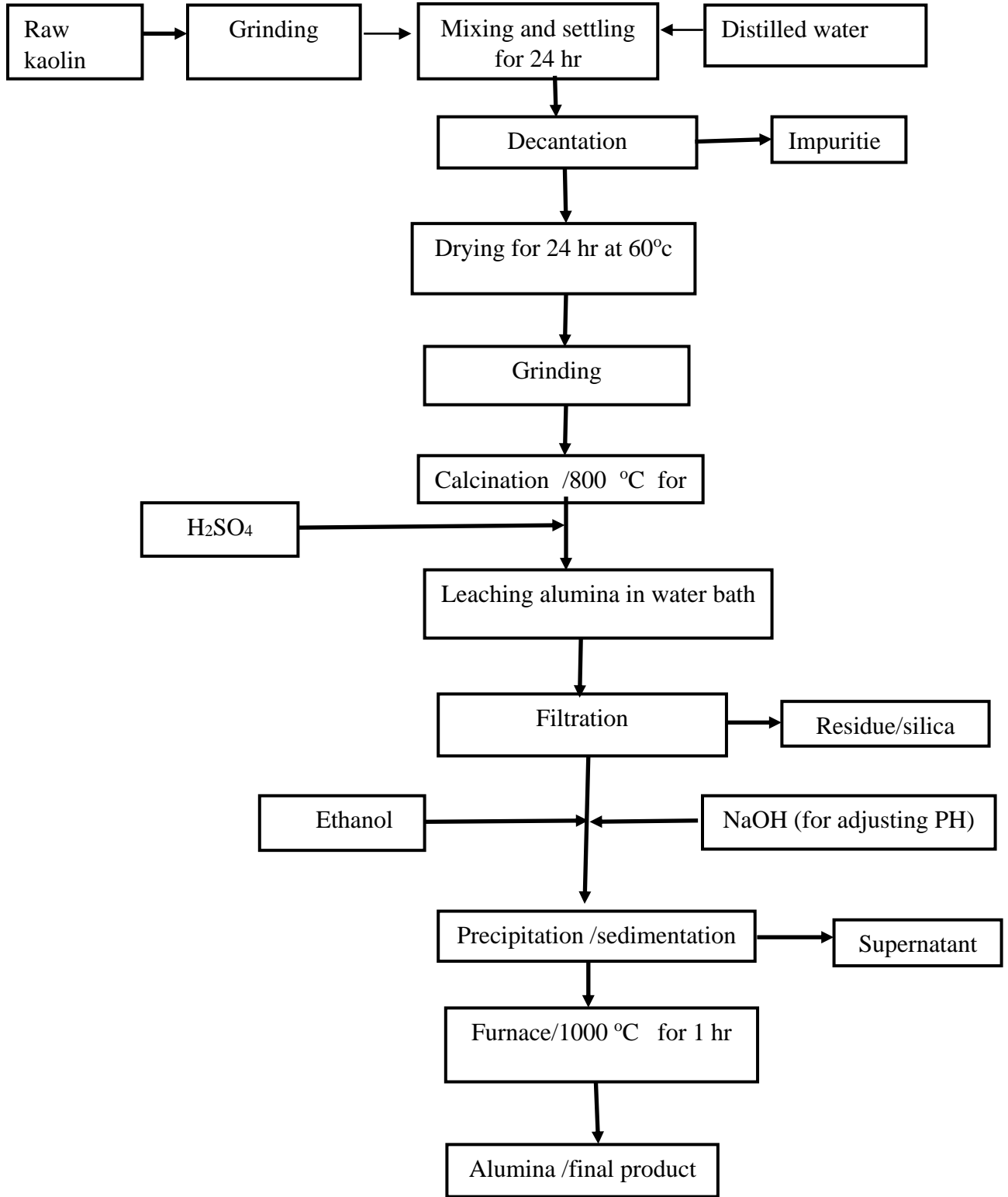
Figure *3*. 4 Process flow sheet for alumina extraction

3.4.1. Clay beneficiation

Naturally, kaolin occurs with impurities which have to be removed for commercial applications, particularly in the paper filling and coating applications as well as in plastic filling. The two principal objectives of kaolin beneficiation are the removal of impurities and production of a desired particle size distribution (Kirabira *et al.*, 2007). The process involved the pre-treatment of raw kaolin to remove impurities. The raw kaolin clay was crushed and ground using wooden mortar and pestle. Then, the ground kaolin was wet – beneficiated into a plastic bucket and mixed with sufficient deionized water. The mixture was stirred and allowed to settle for 24 hours. The fluid above the kaolin was decanted after 24 hours of settling time. These steps were repeated until the decanted water was clear. This process aids in the settling of grit and another heavy mineral while floating of light fractions like mica. The purified kaolin was then oven dried at 60 °C for 24 hr. The dried clay was crushed and sieved with Tyler mesh sieve of mesh size 200 (75 µm aperture opening) so as to further separate the fine grits present in the fraction.

Figure 3. 5 kaolin beneficiation treatment

3.4.2. Calcination

The beneficiated kaolin clay was calcined at 800°C in a furnace for 3 hours. This is for the conversion of alumina content in clay/ kaolin to soluble form and prevents recrystallization of kaolin from mullite (Abdullahi *et al.*, 2013). Kaolin contains quartz, feldspar, mica, colored minerals, soluble salt, and organic matter. The washing process was adjusted to separate clay and silica particles. The washing time was scheduled out by taking into consideration of the peculiarity of the kaolin to be washed and the impurities present (Ara *et al.*). The calcination was carried out at 800 ^{O}C and 98 % H_2SO_4 to have fully calcined kaolin rather metakaolin calcined at an intermediate temperature to remove silicate parts of clay impurities.

3.4.3. Leaching/extraction of alumina

In the extraction process, 18g Sample of calcined kaolin was weighed. 50 % w/w NaOH solution was prepared with deionized water. A 98% H_2SO_4 solution was used to dissolve the alumina content in the calcined kaolin sample in a neck open round bottom flask. The flask was placed in an electric water bath at selected temperature and stirred continuously using a mechanical stirrer. The ratio for calcined kaolin: H_2SO_4 solution was 18g: 300 ml. The extraction was carried out at 3M, 4M, 5M H_2SO_4 solutions at different reaction time of 2hr, 3hr, and 4hr with different leaching temperature of 70, 80, and 90 ^{O}C.

at the end of leaching, the residue which consists mainly of silica was removed and the resulting slurry (supernatant) which is aluminum sulfate was treated with Sodium hydroxide of 50% w/w to adjust the PH between 4.5 and 5.2 for precipitating the aluminum hydroxide easily. Finally, 97 % ethanol was added to coagulate alumina from solution (200 ml of filtered liquor was added of 5ml/min dropwise into 600 ml of ethanol and stirred continuously). The coagulated aluminum hydroxide was dried in an oven at 80 ^{O}C for 6 hr. After drying aluminum hydroxide, it was kept in the furnace at 800°C to form aluminum oxide, $2Al\,(OH)_3 \xrightarrow{\text{800 } ^O\text{C}} Al_2O_3 + 3H_2O$

This aluminum oxide was grinded in a grinder and it was passed through 100 meshes and the final product was obtained.

Figure 3. 6 leaching of alumina

3.5. Characterization of alumina/ kaolin

3.5.1. Fourier Transform Infrared Spectroscopy

The infrared spectrum was recorded by passing a beam of infrared light through the sample. The functional group analysis of the alumina was carried using Fourier-Transformed Infrared (FTIR) spectroscopy (PerkinElmer (4000)). The FTIR spectra were recorded on spectrum (perkinElmer) equipped with KBr beam splitter. Diffuse reflectance system (DRS) was used for alumina samples. IR characterization alumina was performed with PerkinElmer, spectrometer with a frequency range of 4000-400 cm^{-1}.

3.5.2. X-ray Diffraction (XRD)

Alumina sample obtained from c kaolin was subjected to X-Ray Diffraction (XRD) analysis to identify crystalline phases in bulk materials and to determine crystallite size and shape from diffraction peak characteristics. X- Ray Diffraction study was used to find the different phases and crystallography of the elements present in the sample. The source consisted of: Cu-Kα radiation (λ = 1.5405 Å), monochromator on secondary optics, 40 kV power and 35 mA current. Each calcined sample were crushed into fine powder and scanned within the 2θ range of 10–60 $^{\circ}$. The scanning range was maintained at 20 $^{\circ}$ C with

a step size of 0.05 °. The resultant intensity data was analyzed by using in-built diffraction software Match! 3 to monitor the peak position.

3.5.3. Thermo Gravimetric Analysis (TGA)

The thermal stability characteristics of alumina was determined by the thermogravimetric analyzer. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed. The heat treatment was done using temperature programming at heating rate of 20 °C/min starting from atmospheric temperature (25 °C) to 1000 °C. Argon atmosphere was maintained during testing with a flow rate of 2 ml/min to remove all corrosive gases and avoid thermoxidative degradation.

3.5.4. Atomic absorption spectroscopy (AAS)

Atomic Absorption Spectrometry (AAS) is a technique which was carried out for measuring quantities of chemical elements present in kaolin and calcined kaolin by measuring the absorbed radiation of the chemical element of interest. This was done by reading the spectra produced when the sample is excited by radiation. The atoms absorb ultraviolet or visible light and make transitions to higher energy levels (García and Báez, 2012). Lithium metaborate fusion (LiBO2) was used to decompose the samples. A sample of 0.2 g was placed in a platinum crucible and added about 0.6 g of LiBO2. Small string rod was used to mix thoroughly the sample and lithium metaborate. The mixture was fused at 1800 °F (1000 °C) in a muffle furnace for 15 minutes. Atomic absorption methods measure the amount of energy in the form of photons of light that are absorbed by the sample. A detector measures the wavelengths of light transmitted by the sample, and compares them to the wavelengths which originally passed through the sample.

3.6. UPVC pipes production

The polymer and additives were weighed carefully and sent to mixing unit which is stetted at 120℃. High speed mixer mixes the raw materials to get dry blend. The mixture was transferred to a cooling tank automatically and a temperature was reduced to 50℃ rapidly. The cooled product was sent to extruder containing screw and barrel to get the required melting shape by heat, pressure and shear. While passing through the screw, the UPVC particles pass different hating areas for compression, more mixing and gas removing of the

melt. In the last area (after exiting the extruder) the pressure increased to pass the melt through the mold and shaped as the required size and specification. The pipe passed on a fixed speed through calibration and cooling unit by a caterpillar puller. A parallel printer in constant distances marks the size, type, date and so on of the pipes and an automatic saw cuts the pipes in a specified length and a belling machine bells one side of each pipe. After the pupe was produce it was sent to the testing laboratory for quality controls. The final product was ready for further investigation.
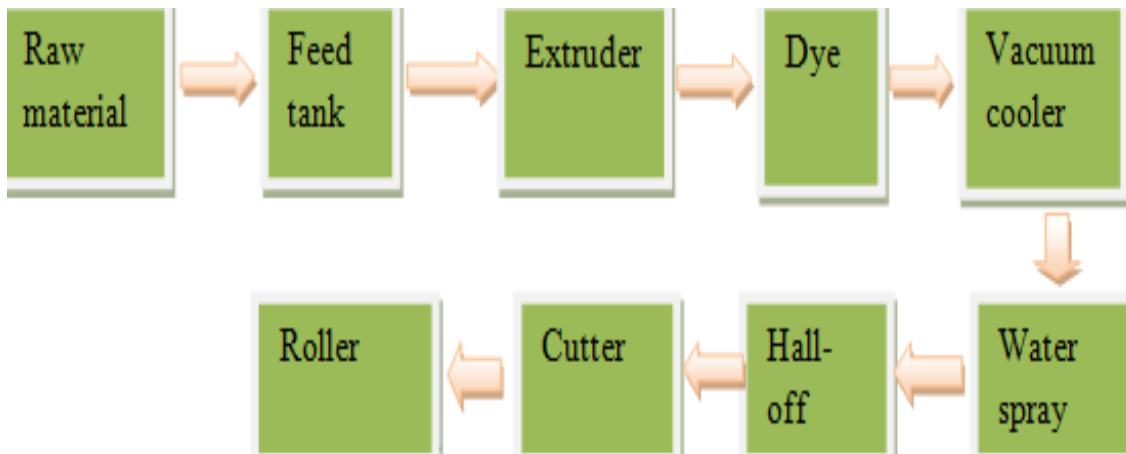
Figure 3. 7 APF UPVC pipe production line

3.7. Characterization UPVC pipes

3.7.1. Thermo Gravimetric Analysis (TGA)

The thermal stability characteristics of UPVC pipes were determined by the thermogravimetric analyzer as described in section 3.5.3.

3.7.2. Tensile strength measurement

The tensile measurements were carried out according to the   ASTM D638 model of 301 using a computerized Universal Tensile   Machine   equipped with suitable   software. It was conducted using an extensometer with a gauge length of 50 mm. In this analysis, tensile properties (tensile strength, elongation and Young's modulus) were   carried out. The samples for tensile test were prepared according to ASTM D638 standard and shapes of samples were like dog-bone. As shown in fig 3.5, specimens were processed through injection molded and brought in standard shape with 3.4 mm thickness. For the analysis, both ends of the specimen were   firmly clamed in the jaws of a universal testing machine.

The jaws were moved apart at rates with a maximum capacity of 5 KN at a cross head speed of 50 mm/min at room temperature with pulling the sample from both ends. The average value of three repeated tests was taken for each material. Finally, Stress was plotted against strain (elongation) to produce a stress-strain curve that describes the materials response to tensile loading.

Figure 3. 8 Universal tensile test machines

Based on **ASTMD638** the specimen was prepared as shown figure 3.5 below.

Figure 3. 9 specimens for tensile test

3.7.3. Flexural strength measurement

Flexural test was carried out using Deepak Universal Tester machine model 301. The test Procedure and test condition was according to ASTM D790. The test procedure used is Test Method 1, Procedure A, i.e., three-point loading utilizing center loading as indicating in figure 3.6. For each material, three samples with a length of 150 mm and width of 40 mm were tested. The samples were tested at speed of 3mm/min and the support span for

the flexural testing is 50mm apart each other. The results of flexural strength were the average of three specimens.
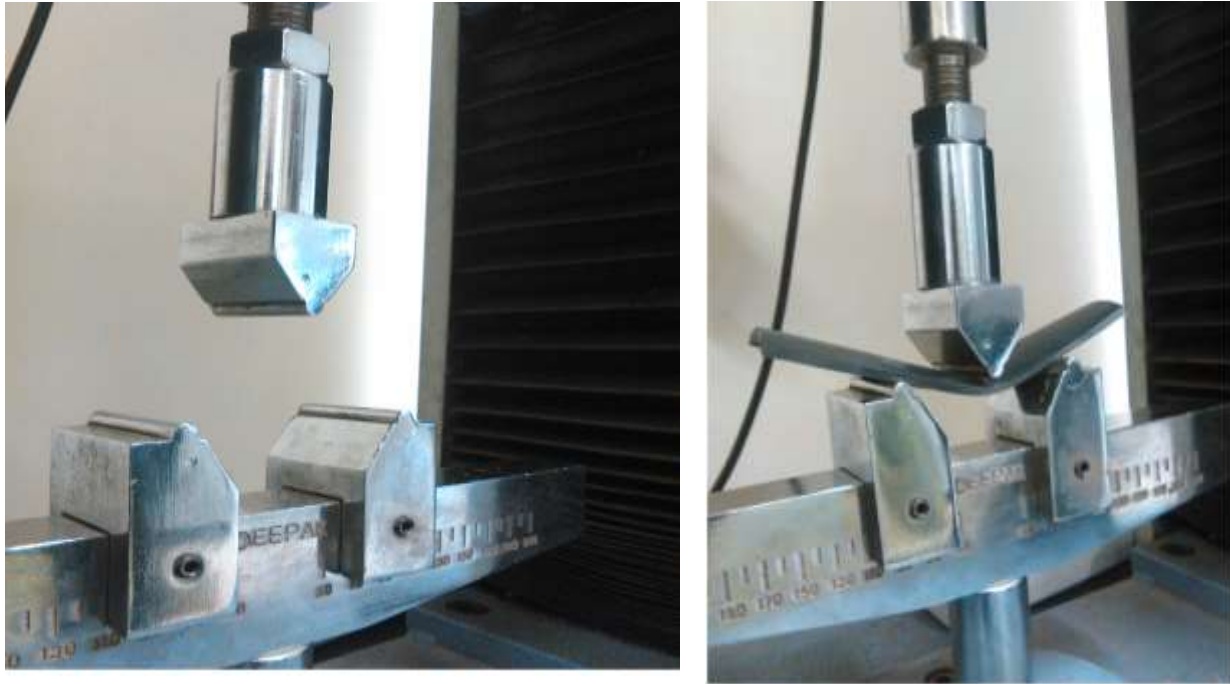
Figure 3. 10 Flexural test machines

3.7.4. Hydrostatic pressure test /burst pressure measurement

The maximum pressure which the pipes can endure before it breaks was measured by hydrostatic (hydro) pressure test method. The 1-meter length of pipe was cut using a saw and burrs of the cut pipe was removed using a knife. The two ends of the pipe were fitted by using end cups and connected with booster. The test was carried out by completely filling the pipe with water by removing the air contained within the pipe. Then the pipe element was subjected to a test pressure that is 1.5 times the design pressure and checked for any leakage. The test pressure was calculated by the following formula;

$P_{test} = 1.5\ P_{max}$, where $P_{max} = 2*S*E*T/D$.

S = specified minimum yield strength at test temperature (kg/cm 2),
T = specified pipe wall thickness minus mill tolerance (cm),
D = outside diameter (cm),
E = quality factor.

The test procedures consist of two steps; the initial expansion and the test phase. When test pressure was applied to a water filled pipe, the pipe expanded. During the initial expansion of the pipe under test, sufficient make-up water was added to the system at hourly duration for 3 hours to maintain the test pressure. After about 4 hours, initial expansion was completed and the actual test was started by adding water to increase the pressure by pump. The result of bursting point pressure was recorded.

3.7.5. Vicat softening test

The immersion bath with the heat-transfer medium at 50 ^{O}C temperature was prepared at the start of the test. The specimen (thickness of 3.4 mm and 10 by 10 mm area) at room temperature was placed, on the specimen support so that it was approximately centered under the needle. The needle was gently lowered without the extra mass, so that the needle rests on the surface of the specimen and holds it in position. The extra mass required to increase the load (50 N) on the specimen was applied. After a 5-min waiting period, the penetration indicator was set to zero. The rate of temperature was increased $50 \pm 5°C/h$. The temperature of the bath was recorded when the needle had penetrated 1 mm into the test specimen. The vicat softening temperature was expressed as the arithmetic mean of the temperature of penetration of all three specimens tested.

3.7.6. Impact Testing Systems

Impact test is undoubtedly the most commonly used test that was done to characterize the ductile to brittle transition behavior in materials. The impact test was done by placing a cylindrical shaped pipe which had 63 mm diameter and 8 cm length for both pipe (filled with alumina and calcium carbonate) specimen at 90 cm height and 15 kg Blow was used. The test was done by dropping the blows from the height (90 cm) of machine onto the specimen until the sample shows fracture sign. The impact value of the material was determined from the energy required to break the specimen. The purpose of impact testing is to simulate these real-life conditions in an effort to prevent the product from breaking, or to make its failure predictable during handling and installation, transportation, and storage in application area when it exposed for different environmental conditions.

3.7.7. Hardness

Among different methods of hardness measurement, the Rockwell hardness test was selected for this study. Initially, a minor load was applied, and a zero-datum position was established. The major load was then applied for a specified period and removed, leaving the minor load applied. As little as a few seconds up to 15 was required for the entire procedure of one sample. The resulting Rockwell number represents the difference in depth from the zero-datum position as a result of the application of the major load. There are several Rockwell scales other than the "B" & "C" scales, (which are called the common scales) for this studies scale B was selected since it related to our products and the force was applied from staring the minor load to the final load of major load on the specimen which had 10 mm length of square shaped and the result was recorded(Koçaker, 2003).

3.7.8. Specific gravity

The test was conducted according to ASTM D792 machines of model (specific gravity tester machine with serial number 0910253) using the water displacement method. The specimen (10 mm square) was weighed in air then weighed when immersed in distilled water at 25°C using a sinker and wire to hold the specimen completely submerged as required. The specific gravity for the three samples was measured and recorded.

3.8. Experimental Design

Investigation of optimal reaction condition to extract alumina general full factorial design was used experiments with two or more factors. It helps to study completely and systematically the interactions between the factors. In addition, it identifies a significant factor. In this study, Design Expert Software version 8 was used to design the experimental factors of arrangement and interactions. In this experiment, reaction temperature, reaction time, and concentration were used as independent input process variables. 54 experiments (3 factors, 3 levels, and 2 replications) were used, the analysis was done to know the interaction effects between the factors and their effect on the yield of alumina and finally the optimum operating condition was selected to produce excess amounts of alumina to manufacturing UPVC pipes.

The pipe production process was carried based on the factory's raw material mixing ratios, (by keeping percentage of raw material constant except the filler one). The mixing ratio of

the factories is (UPVC Resin (100 %), Calcium Carbonate (20%), Stabilizer (5%), and Titanium Dioxide (0.1 %), and Carbon Black (0.025 %). The pipe was produced on the factory's production line.

Table 3. 3 Experimental design of pipe production

Percentage of filler	Type filler and other ingredients	
	Al_2O_3 + others ingredients	$CaCO_3$ + others ingredients
20 %	X	Z
25 %	Y	W

NB. Others ingredients include UPVC resin, stabilizer, titanium dioxide, carbon black

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Model fiting and ANNOVA analysis

The Measure of how efficient the parameters (operating conditions) in the actual response value can be explained by the experimental variables and their correlation is given by R squared values. Several appraisal techniques like the coefficient of determination $R^2 = 0.9258$, coefficients of predicted $R^2 = 0.9035$, adjusted $R^2 = 0.9258$ etc were used to evaluate the adequacy of the selected model (quadratic model) which is suggested by software as shown in table 4.1. Since the R-squared predicted and adjusted are not too far from each other, the better the model in predicting the response.

The value of R^2, which is 0.9258 indicates that 92.58% of the variation in the yield of alumina extraction can be attributed by the three factors (temperature, concentration and time). The correlation of the variable is related to the response (yield) by the following mathematical quadratic model generated by the software.

$$\text{Alumina yield (Y)} = 54.58 + 1.51*A + 2.66*B + 5.48C - 2.82*AB - 0.95*AC - 2.94*BC - 0.29*A^2 - 5.49*B^2 - 0.031*C^2$$

Table 4. 4 Model summary statistics for the response

Source	Std.dev	R^2	Adjusted R^2	Predicted R^2	Press	Remark
Linear	4.31	0.6049	0.5812	0.5358	1089.35	
2FI	3.29	0.7561	0.7561	0.7250	645.35	
Quadratic	**1.81**	**0.9258**	**0.9258**	**0.9035**	**226.82**	**Suggested**
Cubic	1.06	0.9744	0.9744	0.963	86.45	Aliased

In order to calculate the significance of the model (quadratic), the F value test was performed using analysis of variance (ANOVA). From table 4.2 the F value of 74.51 implies that the model term is significant and there is only a 0.0001 % chance that the F value could occur due to noise. Value of " Prob > F " less than 0.0500 indicate that the model terms are significant. In this case, based on the ANOVA table 4.2 below, A, B, C, AB, AC, B^2 are significant model terms.

The F – value of the independent variables A, B, C, AB, AC, BC, and B^2 were estimated as 25.16, 77.56, 329.56, 57.98, 6.6, 63.15, and 110.27 respectively. The model term having the most significant effect on the response is C with F-value of 329.56

Besides evaluating the significance, the adequacy of the model was evaluated by applying the Lack of Fit test. This test is used in the numerator in an F – test of the null hypothesis and indicates that a proposed model fits well or not. The "Lack of Fit F – value" of 25.95 implies that the lack of fit is significant, there is only a 0.001% chance that a "Lack of Fit F-value" could occur due to noise.

Table 4. 5 ANOVA for Response surface quadratic Model

Source	Sum square	Df	Mean square	F_{value}	P_{value} Prob>F	Remark
Model	2202.25	9	244.69	74.51	<0.0001	Significant
A-Time	82.63	1	82.63	25.16	<0.0001	Significant
B-Temperature	254.72	11	254.72	77.56	<0.0001	Significant
C-concentration	1082.30	1	1082.30	329.56	<0.0001	Significant
AB	190.41	1	190.41	57.98	<0.001	Significant
AC	21.66	1	21.66	6.6	<0.0137	Significant
BC	207.39	1	207.39	63.15	<0.0001	Significant
A^2	1.01	1	1.01	0.31	0.5821	
B^2	362.12	1	362.12	110.27	<0.0001	Significant
C^2	0.011	1	0.011	3.47E-033	0.9533	
Residual	144.50	44	3.28			
Lack of Fit	136.17	17	8.01	25.95	<0.001	Significant
Pure Error	8.33	27	0.31			
Cor Total	2364.74	53				

The response values obtained by inserting the independent variable are the predicted values of the model. These values are compared to the actual and experimental values. As it can be seen in fig 4.1 the actual value was distributed relatively near to the predicted value line. This showing that there is a good correlation between the actual and predicted value. This observation shows that the designed quadratic model is well fitted and it can be used to perform the optimization operation for the process.
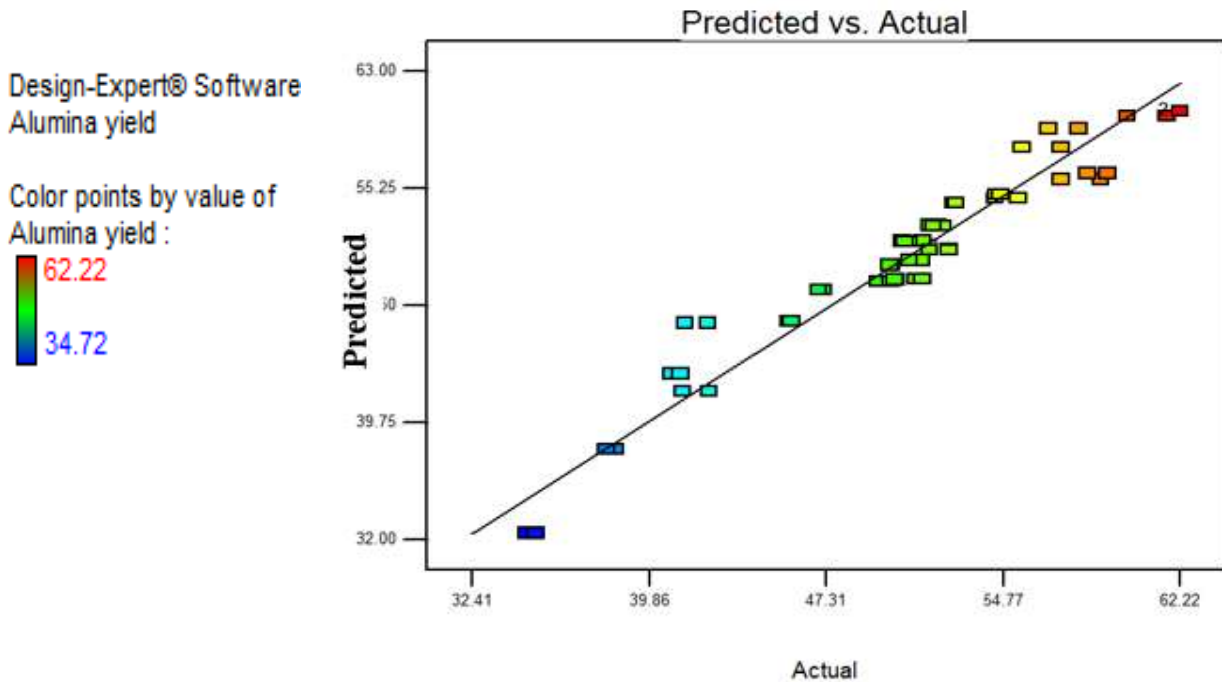
Figure 4. 11 predicted Vs. Actual values of the response

4.2. Parameters effect on aluminia yield

The effect of leaching time (2hr.3hr and 4hr), temperature (70 ^{o}c,80 ^{o}c, 90^{o}c) and concentration of H_2SO_4 (3M,4M, and 5M) on the yield of alumina from kaolin calcined at 800 ^{o}C for 3 hours is shown in the Appendix C. As the result shows that the highest percentage of alumina which is about 62.22 wt. % was obtained at concentration, temperature and extraction time of 5M, 80 ^{o}C and 4 hr, respectively. To explore the most significant factors and the possible interaction which influence the overall efficiency of the dissolution of alumina from calcined kaolin, Design expert software version 7 was used to generate a surface response and statistical data.

4.2.1. Temperature effect

Figure 4.2 depicts the effect of leaching temperature on alumina yield, as shown in the figure below the percentage of alumina yield is significantly affected by leaching temperature. As the reaction temperature increased until it reaches its center value ($80\,^{\circ}C$) it results increasing in the percentage of conversion. This is because when the temperature increases, the kinetic energy of the kaolin-acid solution resulting in increased collision frequency. That comes with higher temperatures which allows the solvent molecules to more effectively break apart the solute molecules that are held together by intermolecular attractions, hence increasing the diffusion rate from the solid bulk phase into the solvent region.

However, the leaching results show extraction efficiency reduction as the temperature is increased above $80\,^{\circ}C$ of center limit. This could possibly be attributed to the precipitation of the aluminum sulphate which was formed at elevated temperatures hence decreasing the diffusion rate.
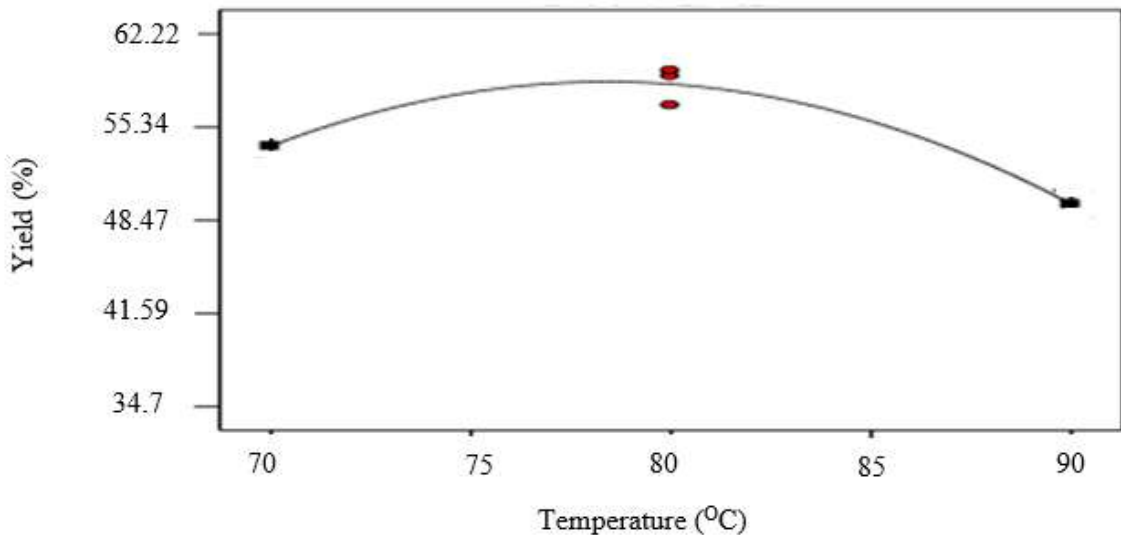

Figure 4. 12 Effect of Temperature on Alumina yield

4.2.2. Time effect

The effect of leaching time on the extraction process is shown in Figure 4.3. The yield of alumina increased with increasing leaching time (a trend of linearly increased as the time extended to 4 hr). The maximum alumina extraction attained after 4hr. Prolonged

32

leaching time allowed ample time of interaction between the acid and kaolin particles (Aderemi et al., 2009). From the results, it can be seen that time has a significant effect on the yield of alumina.
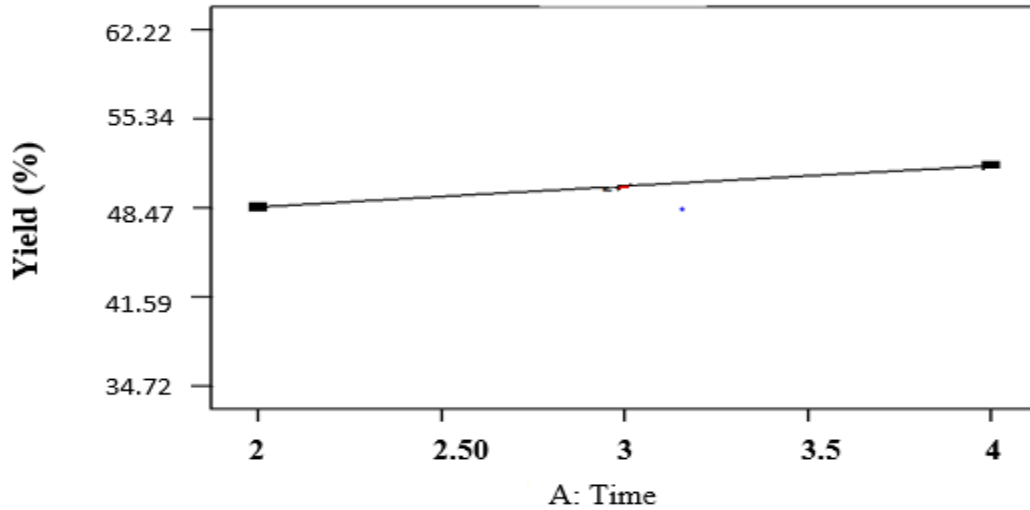
Figure 4. 13 Effect of time on Alumina yield

The effect of Concentration on alumina extraction is illustrated in Figure 4.4. The degree of extraction increased with increase in acid concentration. An increase in acid strength increases the diffusion of H ions into the octahedral layer of kaolin resulting in increased leaching of aluminum ions. A decrease in aluminum sulfate extracted was observed above 5 M H_2SO_4. This is because, increasing the concentration of leaching beyond 5.0 M leads to collapse of kaolin structure and accelerate the formation of alumina sulfate which slow down mass transfer rate across the interface of kaolin (Aderemi et al., 2009).
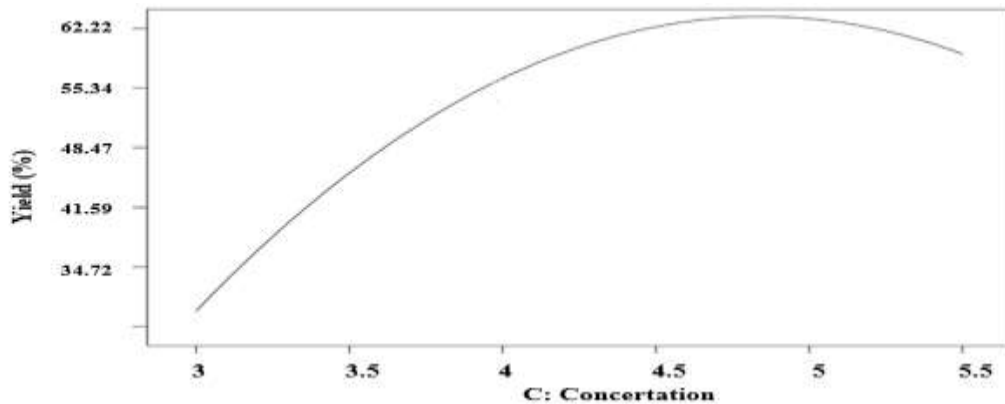
Figure 4. 14 Effect Concentration on Alumina yield

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4.2.3. Interaction effect of temperature and time

The combined effects of adjusting the process variable within the design were monitored using a 3D surface and 2D contour plot. The data presented in figure 4.5 below indicate that the extraction of alumina from calcined clays increases with increasing extraction time corresponding to increment of temperature from 70 °c – 80°c. Based on ANNOV of F - value and figure 4.5 the effects of temperature is relatively higher than time on the yield of alumina, but their combined effect on the alumina yield was very strong.

(a)   (b)
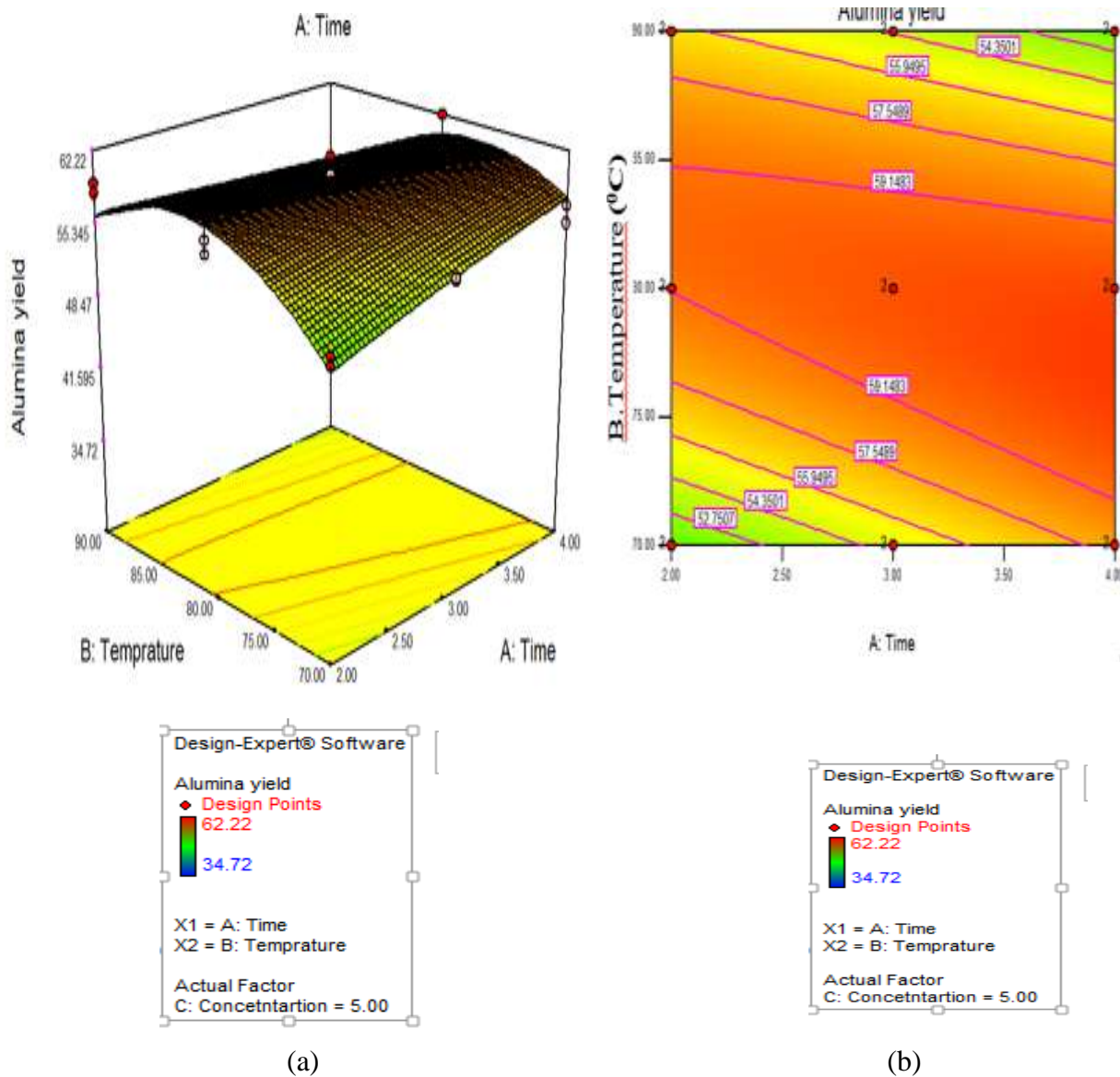
Figure 4. 15 Combined effects of temperature and time on yield on 3D surface (a), and contour (b)

4.2.4. Interaction effect of concentration and time

The data obtained on figure 4.6 indicate that the leaching concentration has an extremely high significant effect than time on the extraction of alumina. A plot of data for the combined effects of reaction temperature and time from figure 4.6 shows that their combined effect is very less significant for the persistent increase in process response of alumina.

(a)   (b)
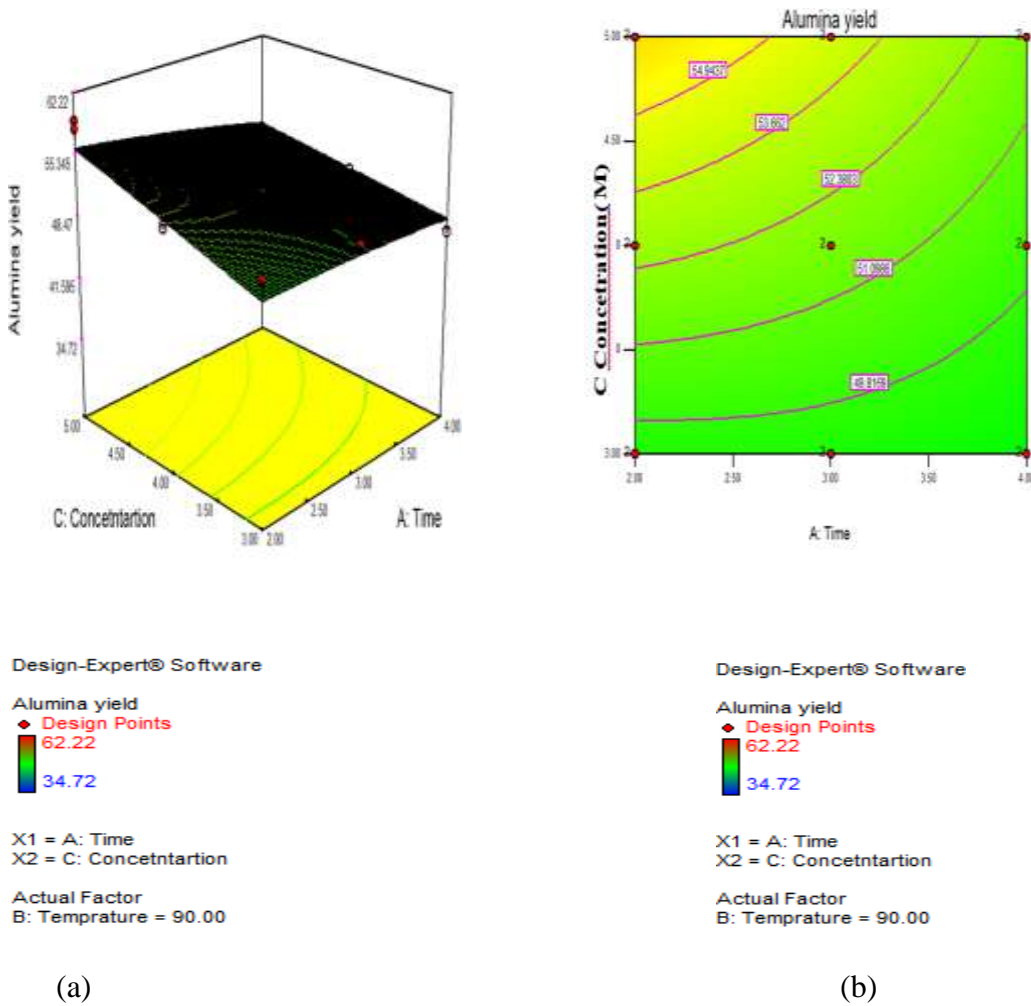
Figure 4. 16 Combined effects of time and concentration on yield on 3D surface (a), and contour (b)

4.2.5. Interaction effect of concentration and temperature

Based on the result shown below in figure 4.7, the effect of concentration and temperature on the yield of alumina have great significant either an individual or combined effect.

Increasing the leaching concentration increases the recovery of alumina until temperature reaches 90°c as seen in figure 4.7. It is expected that the diffusion rate of Al^{+++} from the solid to the solution increase as the concentration and diffusion hydronium ion rise. Increasing the concentration of leaching beyond 5.0 M leads to the collapse of kaolin structure and accelerate the formation of alumina sulfate which slows down mass transfer rate across the interface (Ohale *et al*., 2017).

As the temperature is increased from 70 °c to 80 °c, the yield also increased as the concentration increased correspondingly. The increment of temperature increases kinetic energy which allows the solvent molecules that held together by intermolecular attraction, hence increasing the diffusion rate from the solid bulk phase into the solvent region. However, the leaching results shows extraction efficiency reduction as the temperature is increase above 80 °c . This could be possibly attributed to the precipitation of the alumina sulfate which was formed at elevated temperature.
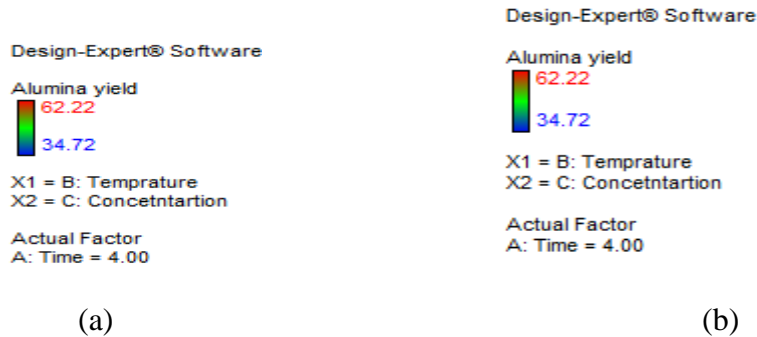
(a)   (b)
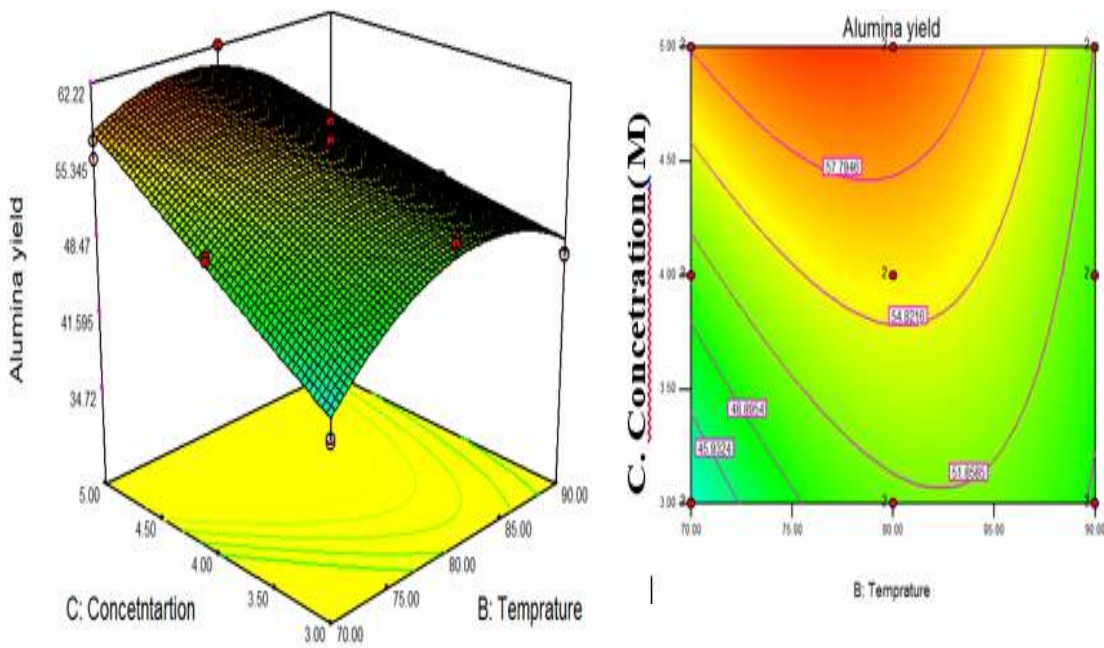
Figure 4. 17 Combined effects of temperature and concentration on yield on 3D surface (a), and contour (b)

4.3.   Alumina Characterization

The extracted alumina was characterized by different instrumental analysis like FTIR, XRD, AABS, and TGA, to confirm the produced product is either alumina or not for the target application area. The raw kaolin also characterized by using XRD and AABS.

4.3.1.   Fourier transform infrared spectroscopy (FTIR) analysis of alumina

FT-IR technique investigates OH vibrations, whose absorption bands appear at different frequencies depending on the cations directly linked to the hydroxyls. This permits the determination of cation distribution around hydroxyls and thus allows assessing short-range cation ordering. The band position is compared with the possible assignments of the samples are presented in the appendix D1and D2. The structure of kaolin minerals consists of a sheet of corner-sharing tetrahedral, sharing a plane of oxygen and hydroxyls (inner hydroxyls) with a sheet of edge-sharing octahedral with every third site vacant (dioctahedral). The general features of the OH stretching absorption bands are well established for kaolin. The band observed at around 3020 cm-1 has been ascribed to the inner hydroxyls, and the bands observed at around the other three characteristic bands are generally ascribed to vibrations of the external hydroxyls. The kaolin sample exhibits the bands near the three characteristic bands at 2157, 2347 and 3000 cm–1 figure 4.8 and figure 4.9. The absorption bands observed at 3000cm–1 and 1105-2347 cm–1 could be assigned to the OH. At a wavelength of 995, it shows that OH linked with Al-based on an appendix reference table. Based on both FTIR graphs the impurities of alumina like quartz, iron, etc has been minimized because the peaks of wavelength start around above 900 cm$^{-1.}$ However the wavelength of Si-O,Fe-O is below 900 cm^{-1}. The Si–Al–Si asymmetric stretching

vibration (1250–950 cm-1) which represents the presence of substituted Al atoms in the tetrahedral. Above 3000 cm^{-1} wave length, Al-OH stretching occurs. Thus, FTIR assures that our sample is the targeted one (alumina).
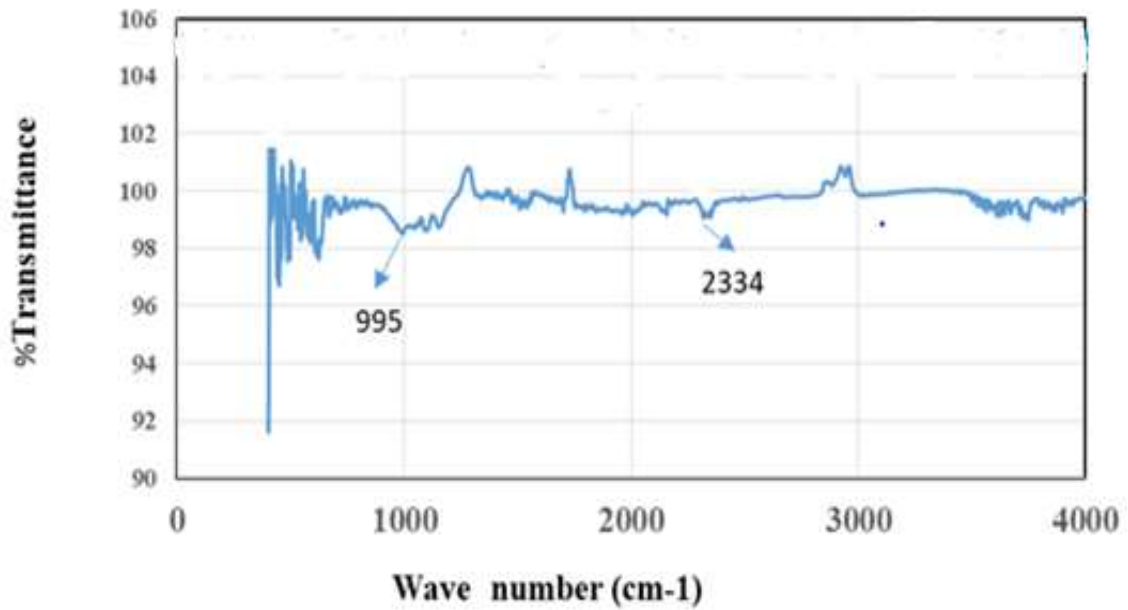
Figure 4. 18 FTIR result for alumina
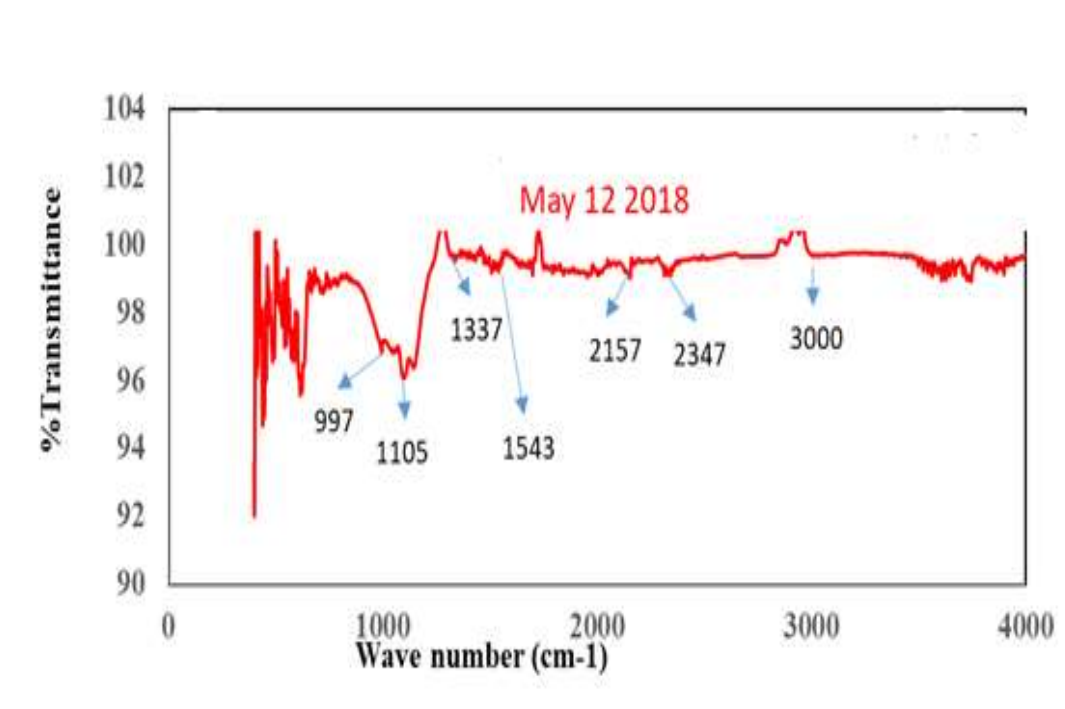
Figure 4. 19 FTIR result of aluminum hydroxide

4.3.2. Atomic Absorption spectra scope (AAS)

The quantitative determination or chemical composition of raw kaolin and the synthesized alumina were analyzed using Atomic Absorption spectroscopy analysis. The alumina and silica result (table 4.3) shows that the leaching process had a great effect on the reduction of silica and other impurities from the raw kaolin and increase the content of alumina. The result is in good agreement with reported by others for both alumina and raw kaolin content (Maifala and Nadiye-Tabbiruka, 2007).

Table 4. 6 AAS of kaolin and Alumina

Sample	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	MnO	P2O5	TiO2	H2O	LOI
Raw kaolin (% wt.)	63.96	23.22	0.88	0.34	0.22	5.06	5.40	0.14	0.13	0.21	0.38	0.43
Leeched Alumina (% wt.)	8.8.0	41.44	0.46	0.18	0.24	20.88	2.30	<0.01	0.03	0.02	0.85	2.41

4.3.3. X-ray powder diffraction (XRD) analysis

As shown in figure 4.10 and 4.11, powder XRD diffractograms were used to characterize raw kaolin and synthesized alumina. The analysis by X-ray powder diffraction was carried out using Cu-Kα1 radiation source of wavelength 1.540598 Å radiation at 1.5 per mint sample scanning rate of 2θ angle within the range of 10 to 60^o to determine morphologies and the degree of crystalline of synthesized samples as well as the kaolin. Amorphous to crystalline transformation was clearly identified. The diffraction pattern of the crystalline compound which analyzed by XRD technique provide information like a well-defined, narrow, sharp and significant peak whereas amorphous materials do not give significant peaks rather the pattern has noise signals, (Das, 2015). After kaolin (amorphous) treatment, several sharp diffraction peaks of great intensity emerge confirming the formation of alumina (crystalline). The XRD pattern of the raw kaolin as shown from the figure 4.10 a peaks were observed about 27.78 , 24.20 , 42.08 whereas , Based on the data which revealed on figure 4.11 about 13 prominent peaks were detected for XRD analysis of extracted Alumina at about 23.22 , 25.65, 31.89, 33.3, 34.12 , 37.95, 39.22, 43.65, 45.2 , 51.71, 53.34, 57.77, 58.89 on 2 theta range . The major peaks of at 2θ also observed for alumina about 25.65, 35.34 43.65, 53.34, 57.77, was the distinctive XRD form of alumna. For both kaolin and alumina, the XRD pattern result is highly agreed with recent finding studies (Laraba, 2006) .Thus, the data presented on figure 4.10 for the XRD value of kaolin has a small zigzag peak, noise peak and luck of lot sharp peak all these are the characteristics of disordered structure or amorphous of the kaolin material. However, sharp and well defined significant major peaks were observed on alumina XRD figure 4.11 which indicates that the leaching out process of alumina from kaolin enables to remove different impurities like quartz, silica, feldspar mica etc, and the synthesized product (alumina) has well-ordered structure or semi-crystal structure.
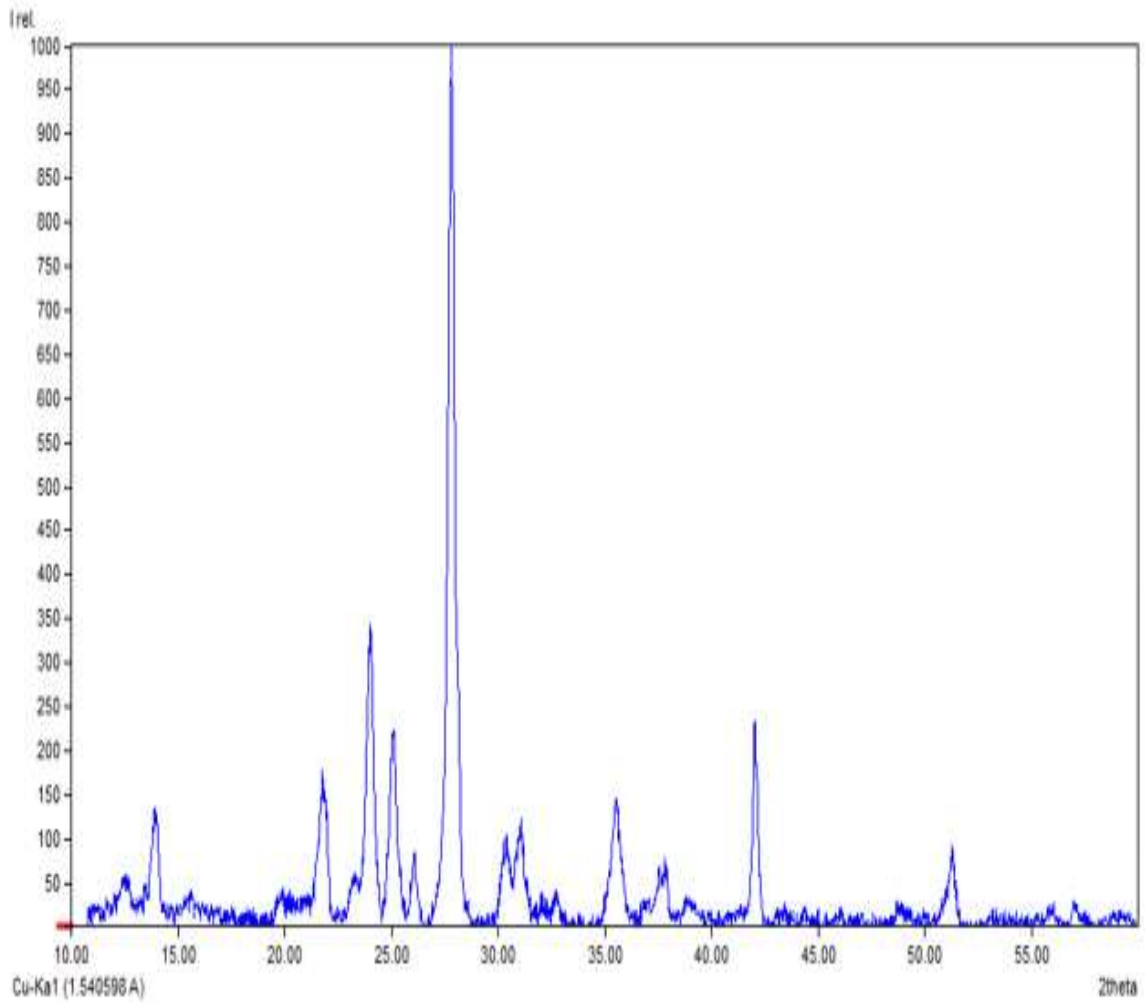
Figure 4. 20 XRD pattern for Kaolin
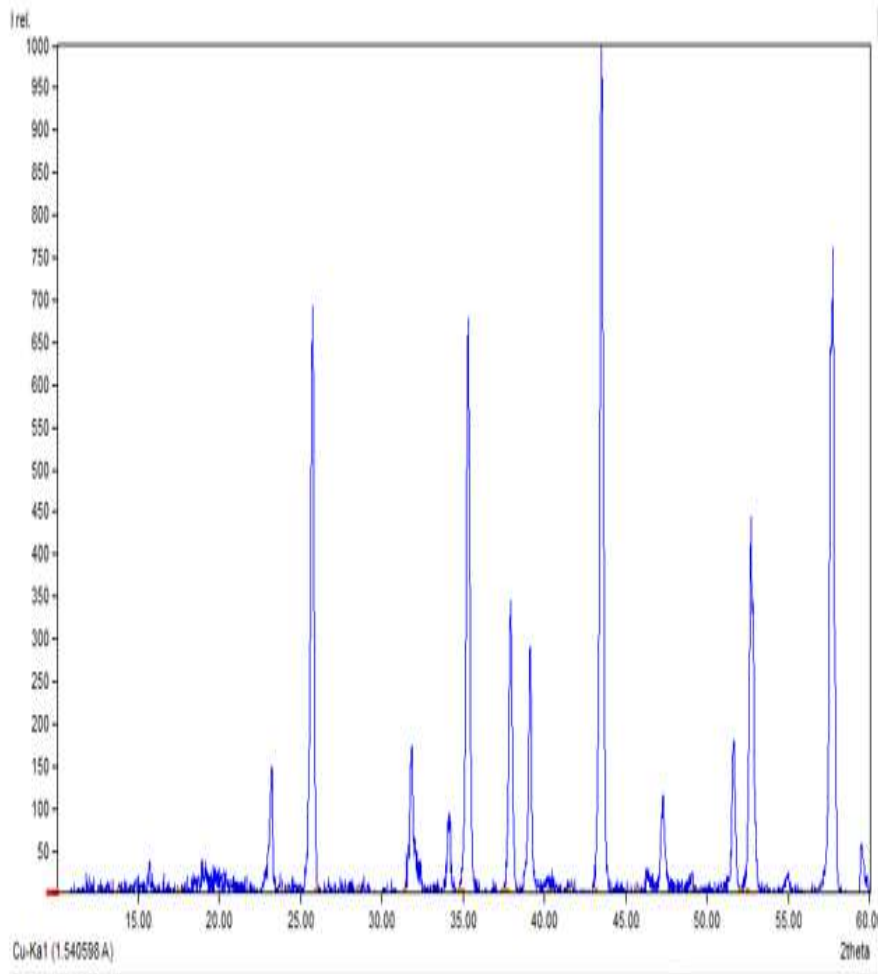
Figure 4. 21 XRD pattern for Alumina

4.3.4. TGA Analysis

The thermal stability of alumina was investigated by TGA analysis. The analysis or heat treatment was carried out from 25 to 1000 $^\text{O}$C at a rate of 10 $^\text{O}$C per min under nitrogen purge atmosphere. Figure 4.12 indicates the loss of primary water (about 5 % weight loss) at a temperature of about 200$^\text{o}$C. It is also interesting to note that about 20 % weight loss occurred within a range of 200 to 650 $^\text{O}$C of temperature. However, immediately beyond this temperature (650 $^\text{O}$C), a sharp decrease in weight was observed due to the decomposition of the structure of the sample, and the range between about 850 to 900 $^\text{O}$C assures the melting temperature of the sample. Thus, the ending temperature had to be at least 964 $^\text{o}$ C but 1000 $^\text{o}$ C was chosen to be sure the pan was completely free of alumna sample. This confirms that when we use alumina as a filler it can provide extreme thermal

stability of material or structurally stable in the application area even when it exposed for high temperature.
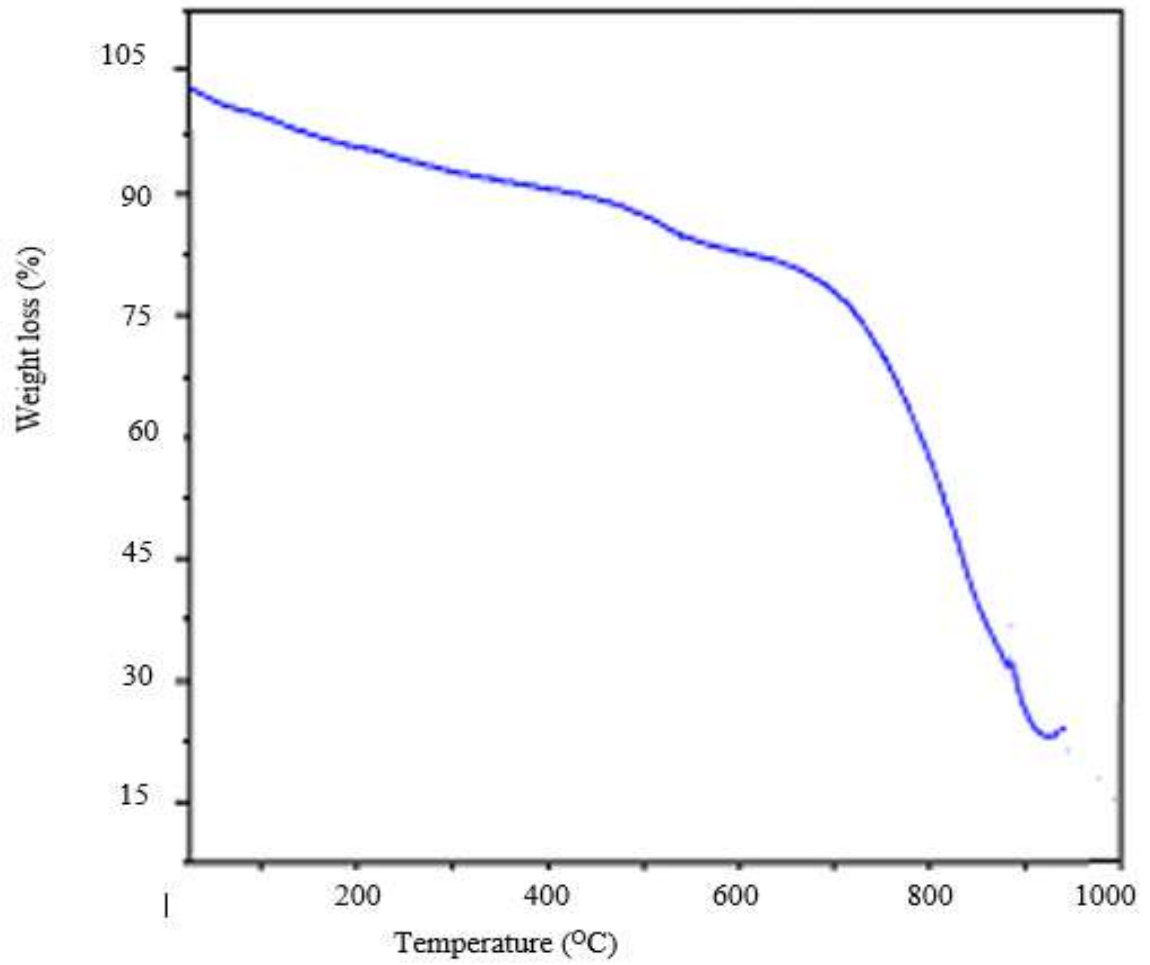
Figure 4. 22 TGA of Alumina

4.4. Analysis of the performance of U- UPVC pipes

4.4.1. Tensile test:

The ability to resist breaking under tensile stress is one of the most important and widely measured properties of UPVC pipe materials used in structural applications. Tension tests were conducted to determine the stress-strain relationships. All tests were made on 63 mm diameter pipes and of thickness 3.4 mm and having similar length and width to make it easier to compare between the two pipes performance in accordance with the ASTM guidelines. Mechanical properties evaluated from the unidirectional tensile stress-strain curve for different UPVC/$CaCO_3$, and UPVC /Al_2O_3 filled pipes are shown in table 4.4 as summarized.

Table 4. 7 summary result of flexural test Modulus and ultimate tensile strength pipe filled with alumina and calcium carbonate

Exper.run with replication	UPVC/20% CaCO3	UPVC/25% CaCO3	UPVC/20% Al2O3	UPVC/25% AlO3
Ultimate tensile strength (Mpa)	2.78	1.95	4.7	5.3
Modulus (Mpa)	2.3	2.5	2.25	2.32
Elongation	15 %	10 %	9 %	11.5%

4.4.1.1. Tensile test of pipe filled with calcium carbonate

In order to analyze the effect of calcium carbonate as filler relative to alumina filler on the mechanical performance UPVC pipe, typically on the tensile strength, 20 and 25 % of CaCO3 were used**.** From Fig. 4.13, the stress-strain curve of 20% incorporated calcium carbonate filler shows that the ultimate tensile strength, stiffens (modulus), and percentage of elongation at the breaking point of the pipe is almost about 2.78, 2.3 Mpa and 15%, respectively. The same trend is observed from figure 4.14, it presents that when the ratio of calcium carbonate increases to 25 % the tensile strength, modulus and elongation are 1.95, 2.5 Mpa, and 10% respectively, by cross-checking the summarized table result of table 4.4. As shown in 4.15, the mechanical performance of the pipe is highly affected by

the contents of calcium carbonate filler. From the initial stages the stress-strain curve for both 20, and 25 % of filler load is proportional to elongation to a certain level (elastic limit), and then increases with elongation to a maximum (uniform plastic deformation), followed by decrease in load due to necking (non-uniform plastic deformation) before fracture of the pipe occurs.

As obviously indicated in the figure 4.15 and Table 4.4, the ultimate tensile strength and elongation of the pipe decreased when the content of calcium carbonate increase to 25 % from 20 %, whereas the modulus is slightly increase corresponding to increments of the filler. The result obtained by this study is consistent with the recently published study by (Klapiszewski *et al*., 2015) who reported that the calcium carbonate filler content increases, the risk the of having agglomerates increases as the filler particles present a strong tendency to agglomerate in a polymeric matrix. The aggregates act as failure-initiation sites. The $CaCO_3$ filler acted as stress raisers leading to the debonding/voiding and the deformation of the matrix material around the nanoparticles. The presence of $CaCO_3$ fillers leads to a higher storage modulus, and this indicates that the rigidity of the composites increased due to the high rigidity of $CaCO_3$ particles. Moreover, the gradual decrease of the tensile strength and elongation at break, in this study, can be related to that at higher filler content, the interaction between fillers and polymer matrix was impeded.
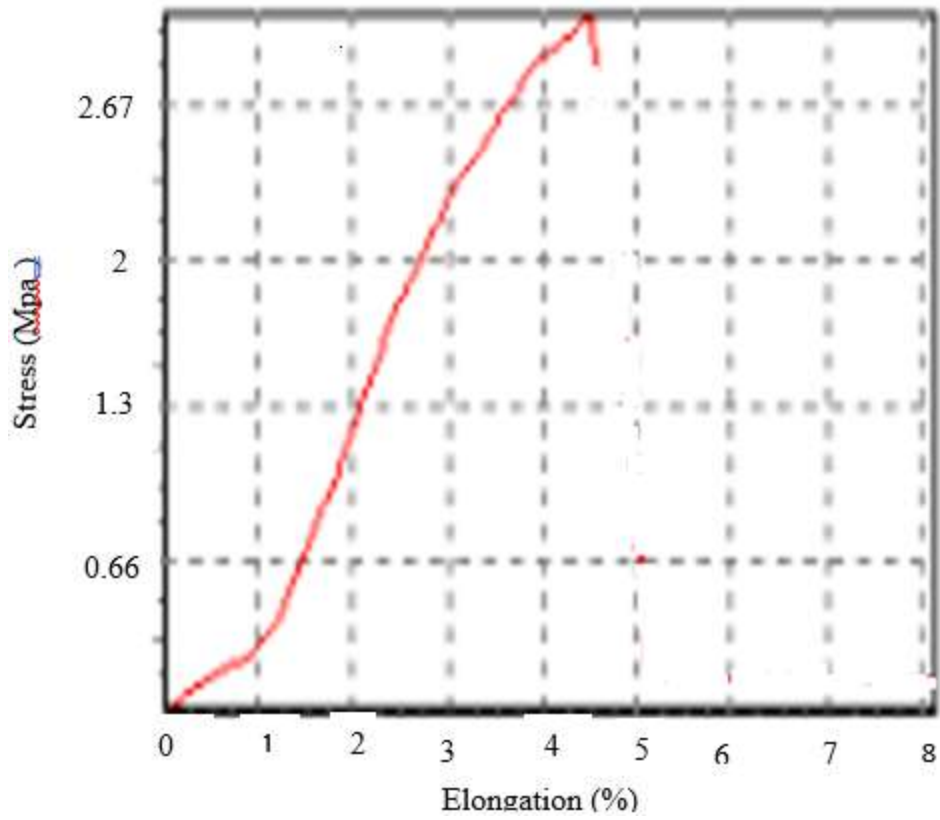
Figure 4. 23 stress –strain for 20 % CaCO$_3$ filled pipe
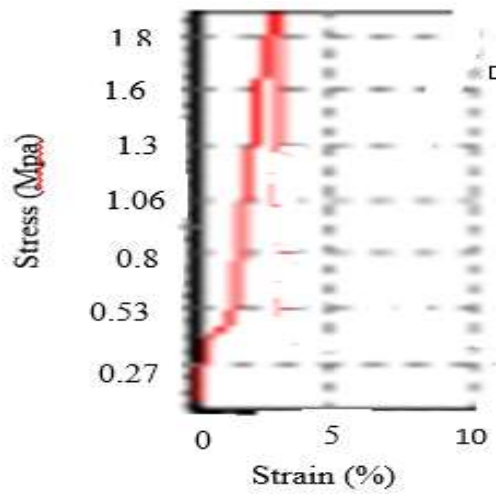
Figure 4. 24 stress – strain curve for 25 % CaCO$_3$ filled pipe
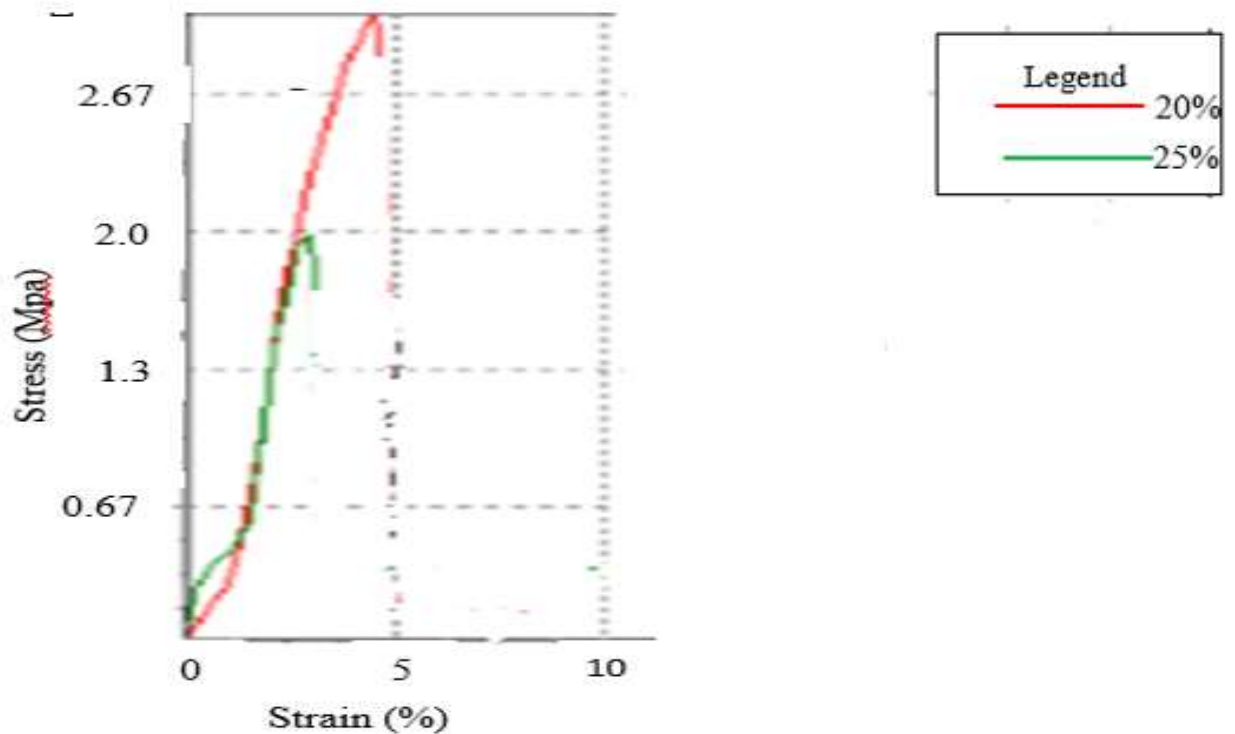
Figure 4. 25 stress-strain curve CaCO$_3$ filled pipe

4.4.1.2. Tensile test of pipe filled with alumina filler

The pipe which is filled with different contents (20 and 25 %) of alumina is shown below on figure 4.16 and 4.17, indeed the curve of stress-strain provides the data how the amount of alumina filler highly influences the mechanical performance like tensile strength, elongation, and stiffens of UPVC pipe. By examining the stress-strain curve of the alumina filled pipe, we can tell that the ultimate tensile strength is increased from 4.7 to 5.3 Mpa , stiffens increase from 2.25 to 2.32 Mpa and also the elongation at break shows slightly increased when the alumina filler content increase from 20 to 25 % of the total weight of the pipe. The same trend which agrees with this study finding was recently found by (Guermazi *et al*., 2016) in their work the reason why the alumina filler enhances the mechanical properties is clearly stated as follows. Alumina is a chemical compound of aluminum and oxygen with strong ionic interatomic bonding, crystalline phase, most stable hexagonal alpha phase giving rise to its desirable material characteristics. Alpha phase alumina is the strongest and the stiffest of the oxide ceramics. Its high hardness, high

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strength, and stiffness excellent dielectric properties and good thermal properties make it the material of choice for a wide range of applications. That is why our study product with alumina shows slightly increment of tensile strength when it compares with calcium carbonate filler products.

When we compare the result obtained from figure 4.16 (20% alumina) and 4.17(25% alumina) the mechanical performance of the pipe filled with alumina shows slight increment in tensile strength than calcium carbonate filled pipe, this may be due to the effectiveness of the filler is highly correlated to shape and size of the particles. The same finding was found by (Guermazi *et al*., 2016) who report that alumina and calcium carbonate have the similar granular shape of particle whereas, in the case of the size of the particle, alumina has 5 µm mean size of particle and calcium carbonate has 57 µm mean size of the particle. Thus, alumina is embedded and dispersed over the polymer matrix without any apparent agglomeration than calcium carbonate due to the size of the particle.
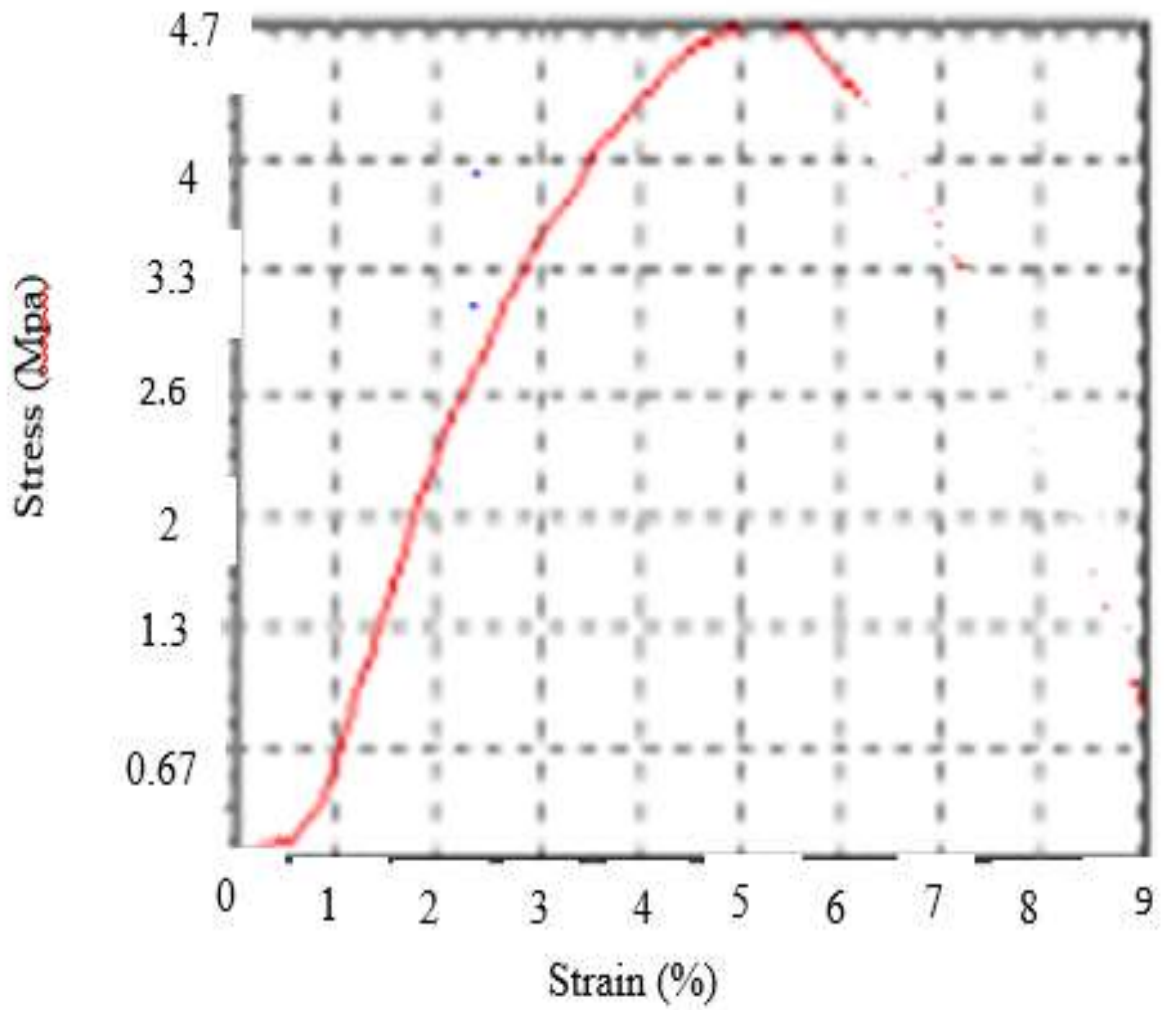
Figure 4. 26 Stress- strain curve for 20 % Al_2O_3 filled pipe
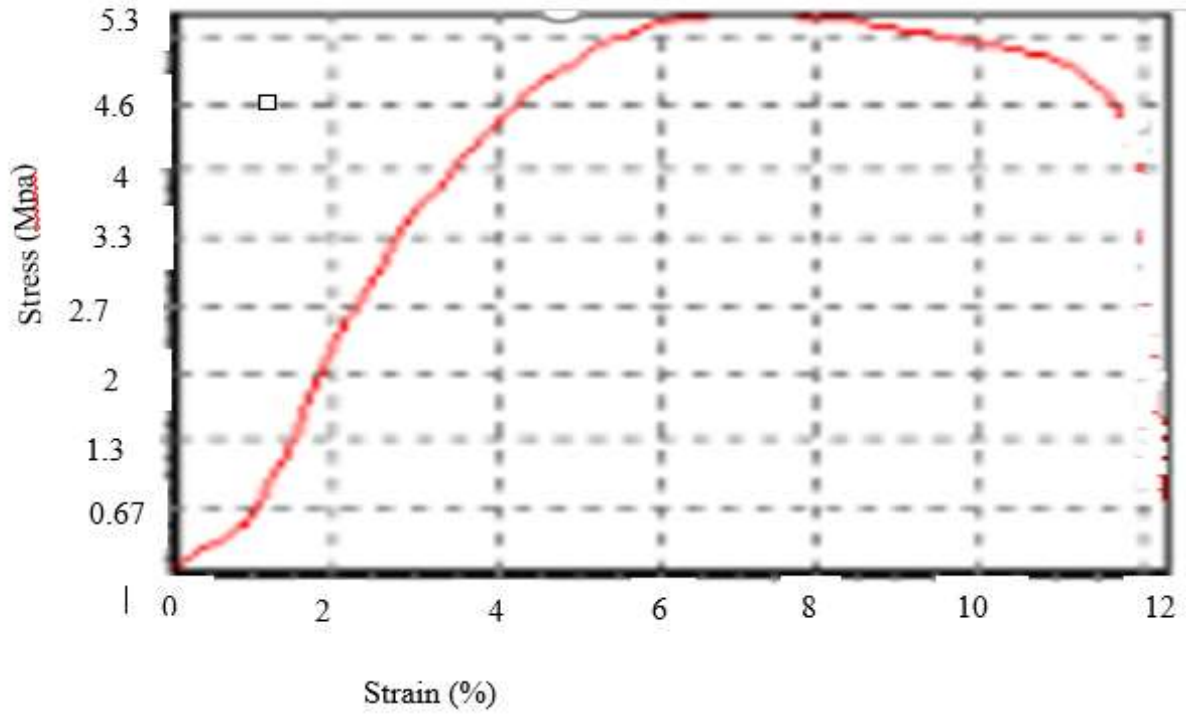
Figure 4. 27 Stress- strain curve for 25 % Al_2O_3 filled pipe
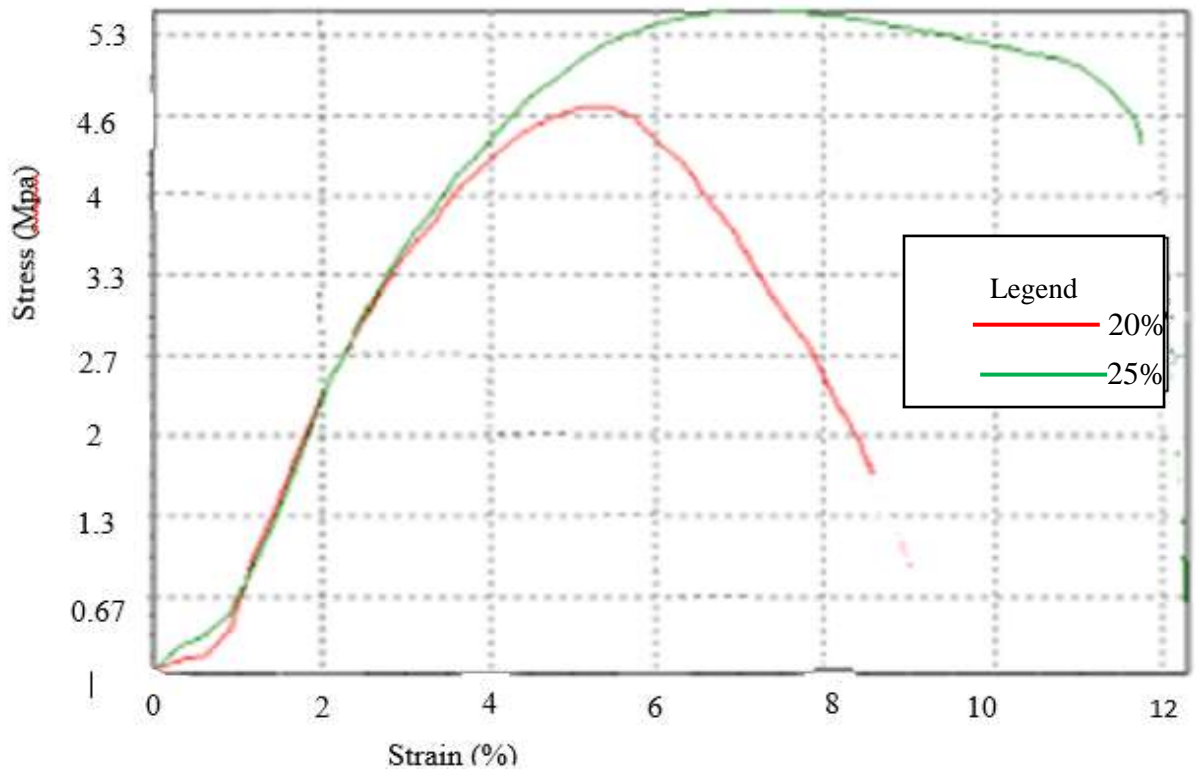
Figure 4. 28 stress-strain curve for Al_2O_3 filled pipe

4.4.2. Flexural test

The effects of calcium carbonate and alumina filler on the three-point bend test flexural strength of the UPVC pipe is illustrated from table 4.5 below. From the result, it is interesting to note that the incorporation of alumina filler into the UPVC pipe was significantly higher than all calcium carbonate filled UPVC pipe. When the weight percentage of calcium carbonate increase from 20 to 25 % the flexural strength of the pipe was decreased to some extent whereas the increment of alumina filler content shows a slight increasing of the flexural strength. It is widely reported by recently published study (HASSAN *et al*., 2009) that show how the flexural strength affected by the fooling reasons The lower values of flexural strength may also be attributed when the content of calcium carbonate increase is due to : incompatibility of the particulates and the UPVC matrix, leading to poor interfacial bonding, to fiber to fiber interaction, voids, and dispersion problems, it also depends on size, shape, type, and loading on filler on material. However, alumina content up to 30% can increase the flexural strength of the pipe when its weight parentage increase.

Table 4. 8 Results of flexural test (in Mpa) pipe filled with alumina and calcium carbonate

Exper.run with replication	UPVC/20 % CaCO3	UPVC/ 25 % CaCO3	UPVC/20 % Al2O3	UPVC/ 25 %AlO3
1	17.9	19.6	22.38	23.5
2	18.26	19.8	22.25	23.65
3	18.1	19.9	22.16	23.8
Average	18.08	19.76	22.27	23.7

4.4.3. Impact performance test

Table 4.6 displays the influence of alumina and calcium filler content on the impact performance of the UPVC pipe. From the test results, it has been found that the resistance to impact loading increases with the addition of filler material. The results also show that impact resistance is more for $CaCO_3$ filled pipe when its percentage of weight increase from 20 to 25% and in a similar fashion the impact resistance for alumina incorporated pipe also shows slightly increment when its content increase by 5% of the weight of

percentage. The reasons what makes the alumina filler reveal some increment of impact energy compared to calcium carbonate is equally agree with recently published article (Sravani *et al*., 2017) which states that ,the reasons for this increase in the impact energies of these alumina particulate filled UPVC pipes are : These are due to having the finest particle size (5µm) compared to $CaCO_3$ (57 µm) which enables to increase the specific surface are of filler to have high interfacial contact area between filler and UPVC matrix ,can resist the propagation of crack.

Table 4. 9 Impact resistance of UPVC pipe filled with Alumina and Calcium carbonate

Sample	Impact energy in KN / 8 cm filler filled pipe			
	UPVC/ 20% wt CaCO3	UPVC/25%wt CaCO3	UPVC /20 % wt Al2O3	UPVC /25 %wt Al2O3
1	2.5	2.7	3.36	4.35
2	2.56	2.82	3.45	4.52
3	2.63	2.78	3.28	4.62
Average	2.56	2.77	3.36	4.50

4.4.4. Hardness test

The hardness performance of the pipe which is filled in different weight percentage of alumina and calcium carbonate is shown below in Table 4.7. This test helps to confirm which type of pipe is highly resisted when it is exposed to cutting and tearing condition in the application area. Based on the result which is shown in the table4.7 pipe filled with calcium carbonate has high hardness value than that of alumina filled pipe. The different hardness value of the pipe is due to the modulus of the filler because hardness value critically depends on the modulus of the filler. The idea of this study is encouraged by the recent finding of (Pain, 2014) who state that hardness is a function of the relative filler content and modulus of the filler . The filler   that increases the moduli of UPVC pipe materials should also increase the hardness of the pipe. Therefore, in his study under tensile test confirms that the pipe which filled calcium carbonate has a higher modulus   than of alumina filled UPVC pipe.

Table 4. 10 Hardness value of UPVC pipe filled with Alumina and Calcium carbonate

Sample	Hardness test (Harden's value) HV			
	UPVC/ 20% wt CaCO3	UPVC/25%wt CaCO3	UPVC /20 % wt Al2O3	UPVC /25 %wt Al2O3
1	65	75.3	56.23	59.28
2	64.25	76.58	55.89	60.48
3	66.23	74.79	57.45	61.27
Average	65.16	75.56	56.52	60.34

4.4.5. Hydrostatic pressure teste

Table 4.8 depicts the result of hydrostatic pressure test performed by using water as the test medium, for the pipe which is filled both by alumina and calcium carbonate. The purpose of these test is to ensure the safety, reliability, and leak tightness of pressure systems of the pipe when it is exposed different environmental condition like underground soil loading (load-bearing capacity) during transporting of drinking water, effluent, and fuel etc conducted safely and effectively. From table 4.8 it is interesting to note that the hydrostatic pressure of the UPVC pipe has been affected by the amount of filler incorporated into the polymer matrix of U UPVC pipe. The ultimate tensile strength of the pipe has a high influence on the pressure test of the pipe this is the reason how the pipe which is filled by alumina reflect the maximum duration of time than calcium carbonate filled pipe. Based on the results finding from the other studies performed proves for calcium carbonate filled beyond 20 % of weight shows a clear reduction in the tensile strain at break is observed correspondingly there is a basic loss of hydrostatic pressure of the pipe or the load bearing capability of the material (Bergström *et al*., 2006) . As stated under the tensile test of this study when the content of filler increases the void and deboning of the polymer matrix with filler is increased typically for calcium carbonate duet to a large particle size of filler compered to alumina.

Table 4. 11 Hydrostatic pressure test and duration of time for pipe filled with filler

Sample (replication)	Hydrostatic pressure test in (bar) and time duration in (hr)			
	UPVC/ 20% wt CaCO3	UPVC/25%wt CaCO3	UPVC /20 % wt Al2O3	UPVC /25 %wt Al2O3
OD (mm)	63	63	63	63
Thickness (mm)	3.4	3.4	3.4	3.4
Length (m)	1	1	1	1
Pressure test (1)	35.0	35.2	35.5	35.36
Pressure test (2)	35.2	35.0	35.24	35.47
Pressure test (3)	35.2	35.0	35.48	35.51
Time duration (1)	0.17	0.13	1.5	1.8
Time duration (2)	0.19	0.11	1.42	1.94
Time duration (3	0.17	0.11	1.38	1.89
Average Pressure test	35.13	35.07	35.41	35.45
Average time duration	0.18	0.12	1.43	1.88

4.4.6. Vicat softening temperature test

The Vicat softening point was a temperature at which a flat-ended needle of 1 mm^2 circular cross-section was loaded with 50 N of the load to penetrate a pipe sample to a depth of 1 mm under 50 ^{o}c rate of temperature rise. The measured result from table 4.9 showed that there is no the same value of Vicat softening temperature for both alumina and calcium carbonate filled pipe both show a slight increase of the Vicat softening temperature this implied that the distribution of filler with the polymer matrix beyond enhancing the mechanical properties of the pipe it also encourage the thermal stability of the UPVC pipe. Thus, the incorporation of the filler into the matrix of UPVC leads to an increase the temperature at which the pipe softened typically, a pipe which is filled by alumina showed high softening point than calcium carbonate because of alumina has a high melting point

of about 2054 ᵒc than that of calcium carbonate which has about 825 ᵒc . As shown from the table 4.12   both pipe filled with alumina and calcium carbonate are on the safety condition particularly alumna filled pipe can withstand at elevated temperature application.

Table 4. 13 Vicat softening temperature

Sample	Vicat softening temperature test in (ᵒc)			
	UPVC/20% wt CaCO3	UPVC/25%wt CaCO3	UPVC /20 % wt Al2O3	UPVC/25%wt Al2O3
1	87.3	90.00	98.23	100.23
2	86	89.69	97.89	101.23
3	86.45	90.10	98.78	101.87
Averae	86.58	89.93	98.30	101.11

4.4.7. Specific gravity

The weight of the produced pipe has a great influence in the application area particularly in the building construction industry due to its load. In this study as we see from table 4.10 below the density of the sample increased with both filler content increased. The main reason for the increment of the specific gravity is, Even though most polymers have specific gravity in the range of 0.9 – 1.4, most particulate fillers have a considerably higher specific gravity in the range of 2.3 to 2.8, thus their incorporation into the matrix of UPVC polymer at specific quantity can increase the specific gravity of the polymer extremely. Typically, alumina filled pipe showed higher density when compared to calcium carbonate filled due to their individual specific gravity difference that is alumina has 3.4 to 3.6 and also calcium carbonate has 2.7 specific gravity thus the specific gravity of their filled pipe depends on their value.

Table 4. 14 Specific gravity measurement

Sample	specific gravity result			
	UPVC/ 20% wt CaCO3	UPVC/25%wt CaCO3	UPVC /20 % wt Al2O3	UPVC /25 %wt Al2O3
1	1.35	1.38	1.48	1.50
2	1.37	1.4	1.46	1.51
3	1.31	1.40	1.48	1.50
Average	1.34	1.39	1.47	1.5

4.4.8. TGA analysis

The valuable information relating to the thermal stability (the material to withstand heating without irreversible changes in its chemical and physical properties) of the UPVC pipe filled with both alumina and calcium carbonate at different weight content was investigated by using thermogravimetric. Heat scanning was performed from 25 ^{o}c to 1000 ^{o}c under nitrogen atmosphere (nitrogen purge with a flux of 50 mL/min) with the heating rate of 10^{o}c/min by the dilatometry machine of Netzsch DIL 402C. The peak of the first derivative indicates the point of the greatest rate of change on the weight loss curve. This is also known as the inflection point.

4.4.8.1. TGA analysis for alumina filled pipe

Based on figure 4.19. (b) TGA curve for 25 % alumina filled pipe reveals that the degradation of the pipe followed a two-step process. The first step of degradation falls in the range of 250 ^{o} C to 500 ^{o}C , this phenomenon is related to oxidation of some impurities and the evaporation of unreacted monomer with the filler at temperatures above the Tg of the UPVC . While the second step occurs in the range of 500 ^{o}C to 900 ^{o}C this related to the crystallinity melting point or melting transition. The first and second –step process mass

depletion is about 45 % and 15 % respectively. The total mass depletion is about 70 % by having 30 % residue from the thermal treatment of the pipe.

The TG graph of 25 % alumina filler at the beginning showed the straight line which confirms that there is no mass change over the range of (0 to 250) ^{O}C. In a similar fashion figure 4.19 (a) 20 % of alumina depict that the onset (depletion) temperature of the degradation started approximately below 100 ^{o}c and 40 % and 35 % mass depletion were occurred until the temperature of approximately 300 and 760 ^{o}c respectively. With the total mass loss of 90 % and 10 % residue. Therefore, comparison of the figure deduces that when the weight ratio of alumina filler increases from 20 % to 25 % the onset temperature of increased correspondingly the mass depletion of the pipe was decreased and it's the implication of thermal stability of the pipe increased when it filled with higher quantities of alumina filler. It is interesting to note that the pipe with a filler ratio of 25 wt% alumina showed a higher degradation temperature than 20 % wt.

(a) 20 % alumina filled pipe   (b) 25 % alumina filled pipe
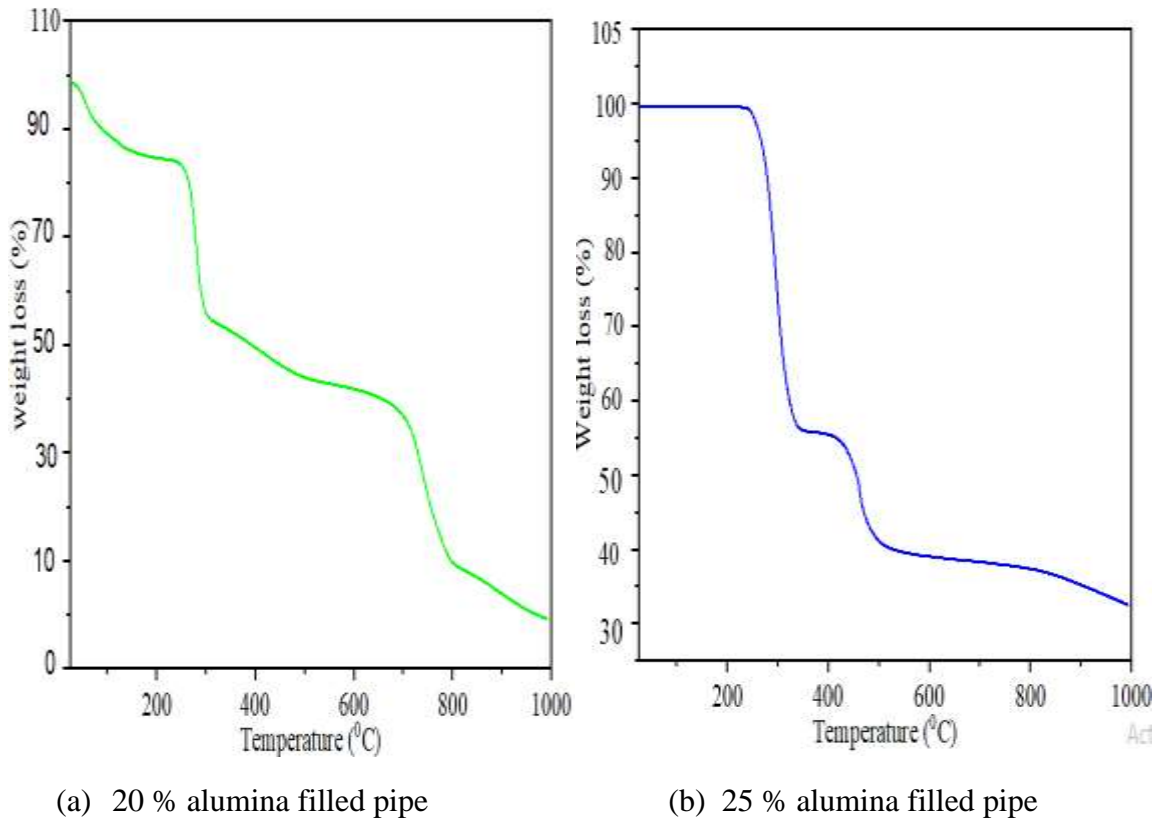
Figure 4. 29 TGA for (a) 25% and (b) 20% of alumina filled pipe

4.4.8.2. TG Analysis for Calcium carbonate filled pipe

The percentage of mass depletion and the degradation of the UPVC pipe filled with 20 % and 25 % of $CaCO_3$ filler is shown below figure 4.20 (a and b) respectively. Even though both graphs show a similar trend, but from the beginning of the graph for 20 wt % of calcium carbonites exhibit extremely sharply downward with approximately 15 % mass depletion and 25 wt % of calcium carbonate reveals smooth downward curve with an approach to 5 % mass degradation. The second stage degradation of the two TG graphs of (20 and 25 % $CaCO_3$) reflect that the mass depletion was approximately up to 650 and 760 ^{o}c respectively. %. The mass depletion is as a result of full decomposition of UPVC and evaporation of some oxides and unreacted monomer with natural particulate substance

Generally, it is obvious to understand that the incorporation of filler (alumina and calcium carbonate) significantly improved the thermal stability of the pipe by increasing the range of degradation temperature and minimizing the mass depletion the result of this study is consistent with previous studies such as (Sultana, 2012) .
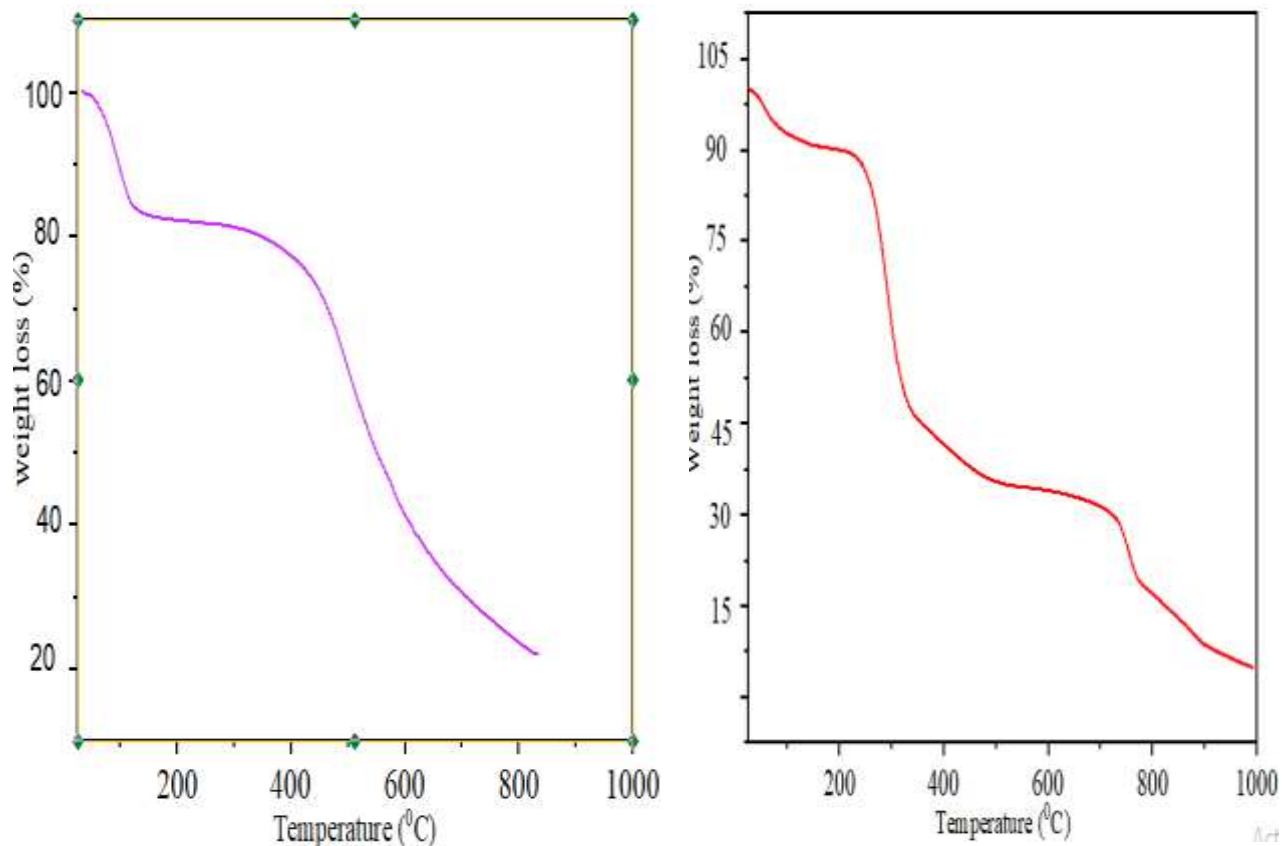
<table>
<tr><td>(a)   20 %wt, CaCO3 filled pipe</td><td>b) 25 % wt of CaCO3 filled pipe</td></tr>
</table>

Figure 4. 30 TG for calcium carbonate filled pipe

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

In this work, the effects of the content of calcium carbonate ($CaCO_3$) and alumina (Al_2O_3) fillers in UPVC matrix and the performance of the UPVC pipe on thermal stability, mechanical properties, and physical properties were experimentally investigated. This study also revealed that the maximum extraction of alumina from kaolin is 62% wt, which is achieved at optimum extraction condition of reaction temperature of 80 °c, 4h, and concentration of 5M of H2SO4 and the FTIR, AAB, TGA, and XRD result confirm that

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the product is alumina. The addition of $CaCO_3$ fillers enhances the material stiffness (the elastic modulus), whereas there was found to be a significant reduction in tensile strength and elongation at break. The flexural strength, hardness, impact and hydrostatic pressure test were enhanced with the incorporation of $CaCO_3$ fillers from 20 % to 25 % wt. As TGA and Vicat softening experiments shows the thermal stability were improved with an increase in calcium carbonate fillers content which promotes the stability of the pipe when it subjected to the high-temperature environment.

In Similar fashion, when a load of alumina filler increases from 20 to 25 %, ultimate tensile strength, flexural strength, impact resistance, hardness and pressure test show an improvement but, the stiffness (modulus and elongation at the break) were decreased. Alumina filler had also a positive effect on the Vicat softening temperature, and on the thermal stability of the UPVC pipe. This property of alumina allows the possibility of the (Al_2O_3) to substitute the common fillers of calcium carbonate without risk of thermal decomposition of the UPVC pipe. In general, as the experimental results shows the effect of the filler highly depends on the amount of filler added for the successful functional properties of the pipe. The results also show that impact resistance, and modulus, were better for $CaCO_3$ filled pipe as compared to the Al_2O_3 filled pipe. However, the ultimate tensile strength, flexural strength, pressure test, hardness, specific gravity Vicat softening were better for alumina filled pipe compared to calcium carbonate filled pipe. When comparing the performance of the pipe for the two filler at the same content i.e. 20 % and 25%, the pipe with calcium carbonate shows higher hydraulic capacity whereas the alumina revealed the higher mechanical performance.

5.2. Recommendation

Although kaolin is widespread in Ethiopia abundantly, it is not utilized for different applications. Therefore, this study confirms that, alumina is suitable as a filler for UPVC pipe production. The extraction of alumina was carried out only by considering operating parameters (leaching time, leaching temperature and acid concentration) but other parameters such as calcination time and temperature, leaching PH and different types of acid concentration needs further investigations. This abundant and local available material

can be further use for other application like membrane, coagulant fertilizer, paper, and zeolite.

It would be advantageous to conduct further research on the filler of alumina by considering the following points which didn't do in this work.

➢ To determine the exact content of the filler it is good to have more than two weight ratios.
➢ Since the performance of the filler highly depends on the size of the particle thus it is recommended to study the particle size distribution by using micro structure as well as scanning electron microscope.
➢ Further study should inquire into the economic feasibility of extraction of alumina from kaolin and used as a filler by substituting calcium carbonate in APF.

6. REFERENCE

Abdullahi, Y., Ali, E., Lawal, A., 2013. Roast alkaline leaching of silica from kaolinitic clay. ARPN Journal of Engineering and Applied Sciences 8, 864-870.

Aderemi, B.O., Edomwonyi, O., Adefila, S.S., 2009. A New Approach to Metakaolin Dealumination. Australian Journal of Basic and Applied Sciences 3, 6.

Al-Zahrani, A., Al Zaitone, B., INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY PRODUCTION OF ALUMINA FROM SAUDI CLAY BY SULFURIC ACID LEACHING.

Aliyu, A., Ahmadu, U., Abdelmalik, A., Sadiq, U., 2016. Preparation of Y-Alumina from Kankara Kaolin in Nigeria by Acid Leaching Using Hydrochloric Acid. Academic Journal Chemistry 1, 8-12.

Ara, H., Zaman, T., Kurny, A., Separation of Silica from Local Clay.

Ayadi, A.J., Soro, J., Kamoun, A., Baklouti, S., Sfax, R., Thomas, A., 2013. Study of clay's mineralogy effect on rheological behavior of ceramic suspensions using an experimental design. International Journal of Research and Reviews in Applied Sciences 14, 374-384.

Bergström, G., Nilsson, S., Thörnblom, K., Ek, C.-G., Herbst, H., Stenström, A., 2006. Durability testing for 100 year lifetime for buried non-pressure plastic pipes, Plastic Pipes XIII Conference, Washington. Citeseer.

Braun, D., 2002. Recycling of UPVC. Progress in polymer science 27, 2171-2195.

Brown, J., 2001. Additives & Compounding. Plastics Additives & Compounding.

Cannon, B., 2009. Investment Opportunities in Mekelle, Tigray State, Ethiopia. Millennium Cities Initiative and Vale Columbia Center Working Paper Series on Investment in the Millennium Cities: New York.

Cheng, H., Zhang, S., Liu, Q., Li, X., Frost, R.L., 2015. The molecular structure of kaolinite–potassium acetate intercalation complexes: A combined experimental and molecular dynamic simulation study. Applied Clay Science 116, 273-280.

Chukwu, G., Ajuamiwe, C., 2013. Investigation of mechanical/physico-chemical properties of kaolinite ore (clay) from Umuariaga-Umudike, Abia State of Nigeria. International Research Journal of Geology and Mining.

Dalen, M., Ibrahim, A., Adamu, H., Nurudeen, A., 2014. Effects of CaCO3 and Kaolin Filler Loadings on Curing Rates of Polyurethane Foams.

Das, S.S., 2015. Preparation & Characterization of Activated Kaolinite.

DeArmitt, C., Rothon, R., 2002. Fillers and surface treatment. Plastics, Additives and Compounding 4, 12-14.

Deka, B.K., Maji, T.K., Mandal, M., 2011. Study on properties of nanocomposites based on HDPE, LDPE, PP, UPVC, wood and clay. Polymer bulletin 67, 1875-1892.

Deshmukh, P.P., 2014. Performance of Large Diameter Polyvinyl Chloride (UPVC) Pipes in Water Applications.

Elias, H.-G., 1984. Additives and Compounding, Macromolecules. Springer, pp. 1123-1146.

Gabriel, L.H., 1998. Service life of drainage pipe. Transportation Research Board.

García, R., Báez, A., 2012. Atomic absorption spectrometry (AAS), Atomic absorption spectroscopy. InTech.

Guermazi, N., Haddar, N., Elleuch, K., Ayedi, H.F., 2016. Effect of filler addition and weathering conditions on the performance of UPVC/CaCO3 composites. Polymer Composites 37, 2171-2183.

HASSAN, A., BAKAR, A.A., WAHIT, M.U., TUEEN, B., 2009. STRUCTURE-PROPERTIES RELATIONSHIP OF HYBRID TALC/CALCIUM CARBONATE FILLED IMPACT MODIFIED UPVC COMPOSITES.

Hounsham, I., Titow, W., 1984. Fillers in UPVC, UPVC Technology. Springer, pp. 215-254.

Keller, W.D., 1964. The origin of high-alumina clay minerals-a review, Clays and Clay minerals. Citeseer.

Kirabira, J.B., Jonsson, S., Byaruhanga, J.K., 2007. Beneficiation and Evaluation of Mutaka kaolin, Proceeding of Second International Conference on Advances in Engineering and Technology, pp. 169-175.

Klapiszewski, Ł., Pawlak, F., Tomaszewska, J., Jesionowski, T., 2015. Preparation and characterization of novel UPVC/silica–lignin composites. Polymers 7, 1767-1788.

Koçaker, B., 2003. Product properties prediction after forming process sequence. METU.

Kunwar, S., 2012. Un-plasticized Polyvinyl Chloride (UPVC) Profiles Production In Nepal: A feasibility Study.

Laraba, M., 2006. Chemical analyses with X-ray diffraction, X-ray Fluorescence and the influence of the impurities on the quality of kaolin of Tamazert El-Milia, Algeria. Journal of Applied Sciences 6, 1020-1027.

Liew, Y., Kamarudin, H., Mustafa Al Bakri, A., Luqman, M., Khairul Nizar, I., Heah, C., 2011. Investigating the possibility of utilization of kaolin and the potential of metakaolin to produce green cement for construction purposes–A review. Australian Journal of Basic and Applied Sciences 5, 441-449.

Luo, J., Jiang, T., Li, G., Peng, Z., Rao, M., Zhang, Y., 2017. Porous Materials from Thermally Activated Kaolinite: Preparation, Characterization and Application. Materials 10, 647.

Maifala, B., Nadiye-Tabbiruka, M., 2007. Chemical and thermal characterization of a clayey material found near Gaborone Dam.

Mekhemer, W.K., Abou El-Ala, A.A., El-Rafey, E., 2000. Clay as a filler in the thermoplastic compounding. Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals 354, 13-21.

Mohanty, A., Srivastava, V.K., Sastry, P.U., 2014. Investigation of mechanical properties of alumina nanoparticle-loaded hybrid glass/carbon-fiber-reinforced epoxy composites. Journal of Applied Polymer Science 131.

Ohale, P., Uzoh, C.F., Onukwuli, O.D., 2017. Optimal factor evaluation for the dissolution of alumina from Azaraegbelu clay in acid solution using RSM and ANN comparative analysis. south african journal of chemical engineering 24, 43-54.

Okpala, C., 2015. Purging mixture for extruder.

Ombaka, O., 2016. Characterization and classification of clay minerals for potential applications in Rugi Ward, Kenya. African Journal of Environmental Science and Technology 10, 415-431.

Pain, R., 2014. Impact: Striking a blow or walking together? ACME: an international e-journal for critical geographies. 13, 19-23.

Peacock, A., 2000. Handbook of polyethylene: structures: properties, and applications. CRC press.

Regassa, L.A., 2016. Synthesis and Characterization of Zeolite A from Kaolin of Ethiopia: Studies of its application as detergent builder and in tannery wastewater treatment. Addis Ababa University Addis Ababa, Ethiopia.

Rothon, R.N., 2002. Particulate fillers for polymers. iSmithers Rapra Publishing.

Sawyer, R., 1967. Determination of dialkyltin stabilisers in aqueous extracts from UPVC and other plastics. Analyst 92, 569-574.

Schulze, D., 2005. Clay minerals.

Sol-Gel, Z., 2005. Chemistry of silicates and aluminosilicates. Ceramics− Silikáty 49, 287-298.

Sravani, K.S., Reddy, B.R.G., Mohammed, R., 2017. Effect of CaCO3 and Al2O3 Fillers on Mechanical Properties of Glass/Epoxy Composites.

Stahmer, M., Whittle, A., 2001. Long term performance of UPVC pressure pipes in a large rural water supply scheme. BOOK-INSTITUTE OF MATERIALS 759, 187-196.

Student, U., Student, P., 2016. EXPERIMENTAL AND THEORETICAL STUDIES ON UN-PLASTICIZED POLY VINYL CHLORIDE (UPVC) PIPE BURIED IN COHESIONLESS BACKFILL. Int J Adv Engg Tech/Vol. VII/Issue III/July-Sept 122, 125.

Sultana, U.K., 2012. Characterisation and beneficiation of Narsingdi clay.

Thabet, A., Mubarak, Y., Bakry, M., 2011. A review of nano-fillers effects on industrial polymers and their characteristics. J. Eng. Sci 39, 377-403.

Thornton, J., 2002. Environmental impacts of polyvinyl chloride (UPVC) building materials. University of Oregon, Cambridge.

Unar, I.N., Soomro, S.A., Aziz, S., 2010. Effect of various additives on the physical properties of polyvinylchloride resin. Pakistan Journal of Analytical & Environmental Chemistry 11, 7.

Underwood, W.S., Bohm, L., 1981. Polyvinyl chloride containing a filler. Google Patents.

Varga, G., 2007. The structure of kaolinite and metakaolinite. Epitoanyag 59, 6-9.

Velde, B., 2000. Clay minerals: a physico-chemical explanation of their occurrence. Elsevier.

Visser, H.A., Warnet, D., Govaert, L.E., Influence of physical ageing on the impact embrittlement of upvc pipes Article Type: Original Research Paper Section/Category: Polymers Corresponding Author: Hendrikus Antonius Visser, Dr. Corresponding Author's Institution.

Weems, J., 1904. Chemistry of clays. Iowa Geological Survey Annual Report 14, 319-346.

Wirawan, R., Zainudin, E., Sapuan, S., 2009. Mechanical properties of natural fibre reinforced UPVC composites: a review. Sains Malaysiana 38, 531-535.

Yahaya, S., Jikan, S.S., Badarulzaman, N.A., Adamu, A.D., 2017. Chemical composition and particle size analysis of kaolin. Traektoriâ Nauki= Path of Science 3.

Yoon, P.J., Han, C.D., 2000. Effect of thermal history on the rheological behavior of thermoplastic polyurethanes. Macromolecules 33, 2171-2183.

APPENDIX

Appendix A: General over view of alumina leaching out from kaolin during laboratory work

Digging of kaolin   washing   preparing for oven drying   oven dry

Leaching   out   and   dry   the   yield

Appendix B: overview of line production of filled pipe and the equipment used for characterization of pipe

Raw material   weighing   mixing

Mixing on production line   extruding (production line)

Final product after extruding

Hydrostatic pressure test machine   pipes before and after bursting by hydrostatic pressure

Vicat softening   impact test machine   hardness test machine   specific gravity

Appendix C: experimental runs by factorial design software and Alumina yield from kaolin

Run No.	H_2SO_4 Conc. (M)	Time (hrs.)	Temp (0C)	Alumina Yield (%)
1	3.00	80.00	3.00	49.5
2	2.00	90.00	5.00	58.33
3	2.00	70.00	4.00	41.28
4	3.00	90.00	3.00	50.28
5	2.00	80.00	5.00	56.67

6	4.00	80.00	5.00	62.22
7	3.00	80.00	4.00	54.44
8	4.00	90.00	3.00	47.22
9	2.00	80.00	4.00	51.67
10	3.00	70.00	5.00	54.5
11	2.00	70.00	3.00	34.72
12	2.00	90.00	4.00	51.82
13	4.00	70.00	3.00	40.83
14	3.00	70.00	4.00	45.72
15	2.00	90.00	4.00	52.22
16	3.00	90.00	4.00	51.39
17	3.00	70.00	3.00	38.06
18	2.00	70.00	5.00	51.67
19	3.00	80.00	4.00	55.42
20	4.00	90.00	5.00	50.83
21	2.00	80.00	4.00	52.03
22	3.00	70.00	4.00	45.87
23	4.00	90.00	4.00	50
24	2.00	80.00	3.00	41.39
25	4.00	70.00	3.00	41.21
26	3.00	90.00	4.00	50.54
27	3.00	80.00	5.00	60
28	4.00	80.00	4.00	57.22
29	3.00	90.00	3.00	50.22
30	3.00	90.00	5.00	52.78
31	2.00	90.00	3.00	51.11
32	2.00	90.00	3.00	51.39
33	2.00	80.00	5.00	57.94
34	4.00	80.00	5.00	62.22
35	4.00	80.00	3.00	52.5
36	2.00	80.00	3.00	42.33
37	4.00	90.00	4.00	50.06
38	4.00	70.00	4.00	50.83
39	2.00	70.00	3.00	35.11
40	4.00	70.00	5.00	55.56
41	2.00	70.00	4.00	42.39
42	3.00	70.00	5.00	54.67
43	4.00	70.00	4.00	51.33
44	3.00	80.00	5.00	61.67
45	4.00	90.00	3.00	47
46	4.00	90.00	5.00	50.64
47	2.00	70.00	5.00	52.5
48	3.00	70.00	3.00	38.44
49	4.00	80.00	3.00	52.5
50	4.00	70.00	5.00	57.22

51	3.00	90.00	5.00	52.67
52	3.00	80.00	3.00	50.06
53	4.00	80.00	4.00	58.89
54	2.00	90.00	5.00	59.17

APPENDIX D1 correlation of FTIR

Wavenumber (cm^{-1})	Assignment
3400	O-H stretching vibrations of hydrogen-bonded hydroxyl groups in polymeric association
2930	Asymmetric aliphatic C-H stretch vibrations–methylene (CH2)
2850	Symmetric aliphatic C-H stretch vibrations–methylene (CH2)
1610	Aromatic ring (C=C in plane) stretching symmetric
1510	C=O stretching vibrations
1458	Asymmetric aliphatic C-H deformation of methylene and methoxyl
1430-1420	aromatic C=C stretching vibrations
1370	Symmetric aliphatic C-H bending of methyl groups CH3
1266	C-O stretch vibration (in lignin-gualacyl ring with C-O stretch)
1224	C-O stretch vibration (in lignin-gualacyl ring and C-O stretch)
1031	C-O-H deformation in cellulose
822	Aromatic out-of-plane-rings with 2 neighboring C-H groups
~534	Si-O-Al^{VI} vibrations (Al in octahedral co-ordination) of clay minerals
~468	Si-O-Si bending vibrations of clay minerals

Appendix D2 correlation table of FTIR for kaolin

Wavenumber (cm⁻¹)							Assignments
Theoritical Kaoline	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	
3670-56	--	--	--	3640	3661	--	Al--O-H stretching
3645	3630	3630	3634	3624	--	3597	OH Stretching, Crystalline hydroxyl
--	3420	3440	3435	3445	3429	3432	H-O-H stretching, Absorbed water
--	2925	2958	2920	2920	2926	2931	C-H stretching
--	2850	2854	2855	2855	2864	2867	C-H stretching
--	--	1875	--	--	1835	--	--
--	1620	1642	1637	1634	1635	1634	H-O-H bending of water
--	--	1520	--	--	--	--	aromatic nitrate
--	1470	1475	--	--	--	--	C-H stretching
--	--	--	1347	--	1356	1360	Al-O as Si cage (TO₄)
1117-05	--	1175	--	1179	1175	--	--
--	--	--	1079	--	--	--	Si-O quartz
1035-30	1038	--	1038	1038	1031	1033	Si-O stretching, Clay minerals
1019-05	--	1005	1008	--	--	--	Si-O stretching
918-09	912	910	--	915	891	893	OH deformation, linked to 2Al³⁺
800-784	840	840	847	--	--	--	OH deformation, linked to Al³⁺,Mg²⁺
--	788	779	797	778	777	799	Si-O quartz
700-686	693	690	--	694	691	696	Si-O quartz
--	--	635	673	--	635	642	Si-O-Si bending
542-35	544	535	535	527	539	543	Fe-O, Fe₂O₃ Si-O-Al stretching
473-68	470	468	470	467	469	467	Si-O-Si bending

Appendix E: Atomic absorption analysis of kaolin (code A) and Alumina (code B) (composition determination)

GEOLOGICAL SURVEY OF ETHIOPIA

GEOCHEMICAL LABORATORY DIRECTORATE

Document Title:	Complete Silicate Analysis Report	Doc_Number: GLD/FS.10.2	Vers
		Effective date:	M

Customer Name:- **Birhanu Ayitegeb**

Issue Date:- 18/12/2018
Request No: GLD/TR/08400718
Report No:- GLD/TR/0827318
Sample Preparation:- 200 Mesh
Number of Sample:- Two(2)

Sample type:- Rock

Date Submitted:- 22/11/2018

Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides

Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

Collector's code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LC
A	63.96	23.22	0.88	0.34	0.22	5.06	5.40	0.14	0.13	0.21	0.38	0.
B	8.80	41.44	0.46	0.18	0.24	20.88	2.30	<0.01	0.03	0.02	0.85	2

Note: - This result represent only for the sample submitted to the laboratory.

NB: - The sample code "**B**" result is violated our test method may be due to the nature of the sample or its sampling so, it ne

Analysts	Checked By	Approved By	Quality
Dessie Abebe			
Tibitna Beletkachew			
Nigist Fikadu	Tadhitu Siraye	Grossa Haile	Neged
Elsa Fesseha			
Wondim Maru			
Yohanis Getachew			
Yirgalem Abriham			