EFFECT OF EGGSHELL AS A FILLER ON THE MECHANICAL PROPERTIES OF FLEXIBLE POLYURETHANE FOAM

BY

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NIGERIA

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NIGERIA**

OCTOBER, 2015

DECLARATION

I declare that the work in this Thesis entitled "Effect of Eggshell as a Filler on the Mechanical Properties of Flexible Polyurethane Foam" was carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

IDRIS MUHAMMAD UMAR

……. …….. …….

Name of Student Signature Date

CERTIFICATION

This thesis entitled "EFFECT OF EGGSHELL AS A FILLER ON THE MECHANICAL PROPERTIES OF FLEXIBLE POLYURETHANE FOAM" by Idris Muhammad UMAR, meets the regulations governing the award of the degree of Master of Science in Chemical Engineering of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Traditionally, calcium carbonate is used as a filler in foam industries and studies have shown that egg-shell contains about 94 % calcium carbonate. The effect of egg-shell in flexible polyurethane foam was studied in this work. Foam with no filler was produced as a control. The egg-shell was beneficiated, characterized and used as filler in flexible polyurethane foam production with varying loads from 5w% to 15 w% at 2.5 w% interval. The effect of various particle sizes on the egg-shell was also studied. Conventional calcium carbonate was also used and the result compared against the produced egg-shell filled foam samples. The produced samples were characterized for compression set, indentation hardness, elongation at break, tensile strength, heat ageing elongation and tensile strength, support factor and density. Scanning electron microscopy (SEM) was also used to study the foam's morphology. The result of beneficiation showed that the amount of $CaCO_3$ increased by 1.355 % after beneficiating the egg-shell. The results indicated that 45 µm particle size egg-shell was better in most of the properties than other particle sizes tested, with values closest to the control. The highest elongation, tensile strength before and after heat ageing were obtained at 5 wt% of egg-shell. The results also showed that the egg-shell filled foams at 63 µm particle size and 5 wt% loading for tensile strength and elongation before and after heat ageing tests were higher than calcium carbonate filled foam by 1.04 %, 2.66 kN/m^2, 0.82 % and 2.22 kN/m^2, respectively. In all cases, the density increase with increase in filler loading and particle size. The SEM analysis showed that cell openings of the produced filled foams decreased as particle size and filler content were increased.

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LIST OF ABBREVIATONS, DEFINITIONS AND SYMBOLS

ABA = Auxiliary blowing agent

A = Area

Al_2O_3 = Aluminum oxide (Alumina)

^oC = Degree Celcius

CC = Mineral calcium carbonate

CaO = Calcium oxide

Cl = Chlorine

Cr_2O_3 = Chromium oxide

Csa = Cross-sectional area

E = Tensile strength

EAB = Elongation at break

ES = Eggshell

EO = ethylene oxide

D = Density

FAO = Food and Agriculture Organization of the United Nations

Fe2O3 = Iron oxide

FCC = Floro-Cloro Carbon

FPF = Flexible Polyurethane foam

(g) = Gram
K_2O = Potassium oxide

kN/m^2 = Kilo Newton per square meter

kg/m^3 = Kilo gram per cubic meter

L = Length

LOI = Lost on Ignition

M = mass

MgO = Magnesium oxide

N = Newton

NIS = Nigerian Industrial Standard

PBW = Parts by weight

Pph = Parts per 100 parts polyol

PO = propylene oxide

PU = Polyurethane foam

S.F = Support factor

SiO_2 = Silicon oxide (Silica)

T = Temperature

TiO_2 = Titanium oxide

t_f = Final thickness

t_o = Initial thickness

V = Volume

W = Width

wt % = weight percent

XRF = X-ray fluorescence

ε = Extension

μm = Micro meter

% = Percentage

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CHAPTER ONE

1.0 INTRODUCTION

A brief review of the research work is given in this chapter.

1.1 Background of the Study

Solid foam is formed when gas is blown through solidifying plastic. Depending on its ability to retain original shape after compression, it can be classified as either flexible or rigid, Isa *et al.*,(2012). The foam can either be closed or open cell foams. In closed cell foams, the foam cells are isolated from each other while the open cell foams are made up of broken cell walls, Babalola and Dominic, (2012).

Flexible polyurethane (PU) foam is one of the major productions from urethane material. Flexible polyurethane foams are used as cushioning material for automotive seat, mattress, furniture, and in packaging etc. According to Klempner and Sendijarevic (2004), flexible polyurethane material has become such widely usedbecause of its excellent light weight, strength to weight ratio performance and the most important is, it offers degree of comfort, protection and utility not matched by other single materials. This usefulness prompts the increase in the prices of polyurethane products consistently over the years which in turn necessitated the incorporation of variety of fillers into foam samples.

Also, the prices of flexible polyurethane foams are becoming increasingly high due to the high cost of raw materials (Onuegbu*et al.*, 2010). The raw materials are mostly liquid reagents and chemicals obtained from petrochemicals and agro-products. The raw materials needed for the production of flexible polyether foam include polyol poly isocyanate, blowing agents, catalysts surfactants and additive such as fillers (Onuegbu*et al.*, 2005).

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Flexible polyether foams are classified as low density, medium density and high density (Ajiwe*et al.,* 2005). The price of foam depends mainly on its density. As a result of the high cost of raw material, there is a need to source for cheaper, a readily available and eco-friendly material that can be used as filler. Filler, as used in plastic and rubber industries is a finely divided solid material which is added to the liquid, semi-liquid or solid composition to modify the physical properties of the composition and to reduce cost (Sharma, 2006).

Predominantly, fillers are used to cheapen end products, in which they are called extenders. Among over twenty most important fillers, calcite ($CaCO_3$) holds the largest market volume and is mainly used in plastic sectors. Other fillers include dolomite ($CaMg(CO_3)_2$), kaolin and talc (Hans, 2005). The use of inorganic fillers have severaldisadvantages including difficulty of preparing and maintaining the dispersion; problems with removal of entrained air; difficulty of mixing and pumping the filler/polyol slurry; loss of the foam physical properties; difficulty of processing on all types of foam machinery, and, due to their abrasive nature, increased wear on machinery components (Bartczak*et al.,* 1999).

In recent time there is growing efforts to develop new classes of bio-inspired composite materials. The main advantage of these types of materials is that they are environmentally friendly and do not contribute to the depletion of energy resources because they are derived from renewable resources (Toro *et al,* 2007). However, previous studies have proved that chicken eggshell (ES) is an agriculture byproduct that has been listed worldwide as one of the worst environmental problems. This eggshell contains about 95 % calciumcarbonate in the form of calcite and 5 % organic materials such as type X collagen, sulfated polysaccharides, and other proteins (Hassan *et al.,* 2012), which makes it a rich source $CaCO_3$ as well as being environment friendly, biodegradable, available and low density. These characteristics qualify eggshell as a

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good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories. Although there have been several attempts to use eggshell components for different applications, its chemical composition and availability makes eggshell a potential source of filler in polymer composites (Abdullah et al., 2011).

More so, the eggshell has been used as reinforcement in polymer composites. Some of the works carried out on the use of eggshell in polymer composites are: Patricio Toro et al., (2011), studied eggshell, a new bio-filler for polypropylene composites. The work proved that eggshell composites showed lower modulus of elasticity values than talc composites, talc filler could be replaced by up to 75 % with eggshell while maintaining a similar stiffness and modulus of elasticity compared to the talc composites. Beside the work reported above on eggshell which was used in polypropylene, the use of eggshell to fill polyurethane foam has not been reported to the best of our search. This research work is therefore, targeted at exploring other source of calcium carbonate particularly the organic substance with special interest in $CaCO_3$ from eggshell.

1.2 PROBLEM STATEMENT

High cost of raw materials used for the production of polyurethane foam especially polyol and isocyanate, demands sourcing for a cheaper, readily available and eco-friendly material that can be used as filler.

Mineral calcium carbonate ($CaCO_3$) holds the largest market volume in the plastic sector and is mainly imported. Hence, theneed to source for renewable materials, which can serve as

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alternative fillers to the conventional mineral calcium carbonate ($CaCO_3$) with a view of minimizing the polyurethane foam production cost.

The annual egg production in Nigeria is estimated at 552,994.32561 metric tonnes (552,994,325.61kg). And the eggshells disposal poses a significant challenge to these industries in this time of increasing environmental safety which have necessitated the need to utilize these eggshells as fillers by polymer industries.

1.2 JUSTIFICATION

Eggshells have been identified to contain up to 94 % $CaCO_3$ which make them suitable for used as filler in polyurethane production. In addition, eggshells have been confirmed to be readily available.

The use of eggshell in the foam production if established will provide means of cleansing the environment of pollution problem which the eggshells constitute and also provide alternative use for the eggshells.

It usage will also, provide an alternative to the predominantly used mineral calcium carbonate, hence reduce its importation.

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1.3 AIM AND OBJECTIVES

The aim of this research work is to investigate the effect of eggshell on the mechanical properties of polyurethane foam. This aim was achieved via the following objectives:

1. To improve the $CaCO_3$ content by means of eggshell beneficiation.
2. Produce polyurethane foams using the improved eggshell as filler for properties modification.

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3. And to establish the extent of properties modification.

1.4 SCOPE

The scope of the work covers the collection and beneficiation of eggshells, production of flexible polyurethane foam using eggshell as filler at different loadings and particle sizes.

Production of flexible polyurethane foams using mineral calcium carbonate ($CaCO_3$) at industrial filler loadings and particle sizes.

Characterization of the eggshells and produced foams, then compare the results obtained with those available in literature.

CHAPTER TWO

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2.0 LITERATURE SURVEY

Brief historical background and literature on polyurethane foam is reviewed and presented in this chapter.

2.1 Introductionand Background Theory

Polyurethanes, also known as polycarbamates, belong to a larger class of compounds called polymers. Polymers are macromolecules made up of smaller, repeating units known as monomers. Generally, they consist of a primary long-chain backbone molecule with attached side groups.Polyurethanes are linear polymers that have a molecular backbone containing carbamate groups (-$NHCO_2$) (Kaushiva and Wilkes, 2000). These groups, called urethane, are produced through a chemical reaction between a diisocyanate and a polyol.

Polyurethane first developed in late 1930s according to Kaushiva and Wilkes (2000), are some of the most versatile polymers. They are used in building insulations, surface coatings, adhesives, solid plastics, and athletic apparels. The production of foam, which is a member of the family of polymeric compounds, began with latex as the major raw material in the early thirties. The first foams were produced using polyester alcohols but were unable to withstand in-door temperature and humidity conditions. They also often failed by crumbling away; as a result they were quickly replaced by polyurethane foams made from polyether polyols (Babalola and Dominic 2012). Polyurethane chemistry was first studied by the German chemist, Friedrich Bayer in 1937. He produced the early prototypes by reacting toluene diisocyanate with dihydric alcohols. From this work, one of the first crystalline polyurethane fibers, Perlon U, was developed (Babalola and Dominic, 2012).

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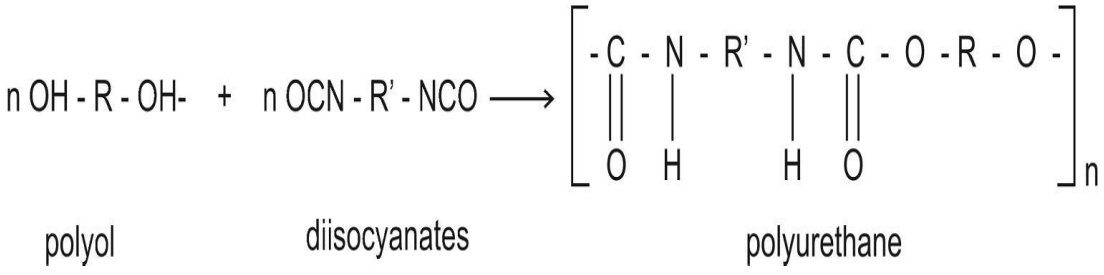
Furthermore, the development of elastic polyurethanes began as a program to find a replacement for rubber during the days of World War II. In 1940, the first polyurethane elastomers were produced. These compounds gave malleable gums that could be used as an adequate alternative to rubber. When scientists found that polyurethanes could be made into fine threads, they were combined with nylon to make more lightweight, stretchable garments (Kaushiva and Wilkes, 2000).In 1953, the first commercial production of flexible polyurethane foam was begun in the United States of America (Kaushiva and Wilkes, 2000). This material was useful for foam insulation. In 1956, more flexible, less expensive foams were introduced (Kaushiva and Wilkes, 2000). During the late 1950s, moldable polyurethanes were produced. Over the years, improved polyurethane polymers have been developed including Spandex fibers, polyurethane coatings, and thermoplastic elastomers (Kaushiva and Wilkes, 2000).Foam production technology was introduced to Nigeria in 1964 (Makanjuola; 1998) and since then there has been tremendous improvement which has made polyurethane foam a versatile and high quality cushioning material suitable for several purposes.

2.2 Polyurethane Foams

Polyurethane foams are made up of solid-gas composites in which the continuous solid phase provides structural and mechanical characteristics such as hardness, resilience, load bearing ability, compressibility and containment for the gas phase (Babalola and Dominic, 2012). Polyurethane foams are chemically complex materials formed by the reactions of liquid starting ingredients (isocyanate and polyether polyol). The foamy structure results from the release of carbon dioxide bubbles generated by a reaction of water with the isocyanate (Umar, 2010). Synthetic polymers, like polyurethane, are produced by reacting monomers in a reaction vessel.

`

In order to produce polyurethane, a step also known as condensation reaction is performed. In this type of chemical reaction, the monomers that are present contain reacting end groups. Specifically, a diisocyanate (OCN-R-NCO) is reacted with a diol (HO-R-OH).



1.1

The first step of this reaction results in the chemical linking of the two molecules leaving a reactive alcoholon one side and a reactive isocyanate (NCO) on the other (Equation 1). These groups react further with other monomers to form a larger, longer molecule. This is a rapid process which yields high molecular weight materials even at room temperature. Polyurethanes that have important commercial uses typically contain other functional groups in the molecule including esters, amides, or urea groups (Kaushiva and Wilkes, 2000).

2.3 Flexible Polyurethane Foam

Flexible polyurethane foam is a product of polymerization of polyol, toluene diisocyanate, water, dimethylethanolamine, methylene chloride, silicone and stannous octoate and can be classified into three based on density (Ajiwe*et al.*,2005; Onuegbu*et al.*, 2010).

Again, the flexible foams have relatively low load bearing properties but on the other hand with high recovery properties compared to the semi rigid and rigid foams. In addition, flexible polyurethane foams could range widely in terms of softness or firmness, resilience, density and

`

others; and flexible foams could also be utilized in various applications including furniture, packaging, and automotive.

Moreover, flexible polyurethane foams were made in either slab stock or molded form. In slab stock production, large slabs were made in a long and continuously pour lasting for an hour or more while themolded flexible foams were made when a large number of relatively small parts are required, for example, when inserting required wires, fabrics or making composites to reduce the cost of materials and other complicated configurations (Onuegbu*et al.*, 2010).

However, the flexible polyurethane foams are divided into two groups; polyester- based foams and polyether-based foams. Polyester foam is widely manufactured in Nigerian Polyurethane industries (Makanjuola, 1999).These two kinds of foams are contrasted in Table 2

Table 2.1: Contrast between Polyester and Polyether Foams (Makanjuola, 1999).

Polyester Foams	Polyether Foams
Rigid foams which are easily crumbled	Flexible foams with more workability
Production is carried out using a relatively complicated and expensive high-pressure machine	Production is carried out using a simple low-pressure machine
Pre-mixing of chemicals before production is required	Chemicals are metered separately and mixed during production
Higher cost of production	Lower cost of production
Possesses poor elasticity	Possesses better elastic quality

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2.4 Flexible Polyurethane Foam Chemistry

This section focuses on the basic chemical reactions involved in the formation of flexible polyurethane foams. Since flexible polyurethane foam production requires a variety of chemicals and additives, this section will review specific chemicals and their importance in the foaming process.

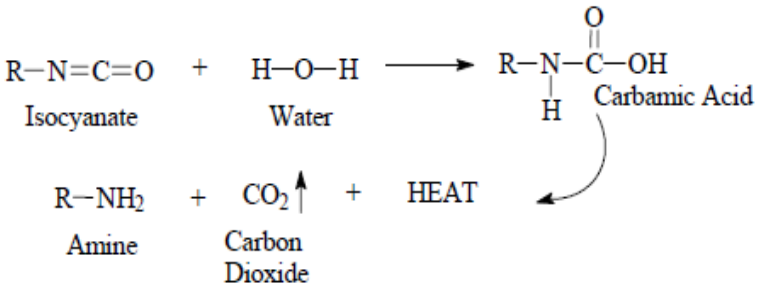
2.4.1 General Chemical Reactions

Flexible polyurethane foam chemistry features two reactions:The 'blow' reaction and the 'gelation' reaction. A delicate balance between the two reactions is required in order to achieve foam with a stable open-celled structure and good physical properties. The commercial success of polyurethane foams can be partially attributed to catalysts which help to precisely control these two reaction schemes. An imbalance between the two reactions can lead to foam collapse, serious imperfections, and cells that may open prematurely or not at all (Kaushiva and Wilkes, 2000).

2.4.1.1 Blow Reaction

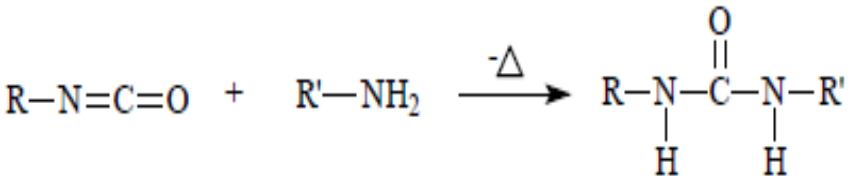
The first step of the model blow reaction (Equation 2) involves the reaction of an isocyanate group with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat. In the second step (Equation 3), the newly formed amine group reacts with another isocyanate group to give a di-substituted urea and additional heat is generated. The total heat generated from the blow reaction is approximately 47 kcal per mole of water reacted, along with the carbon dioxide released in the first step and serves as the principal source for 'blowing' the foam mixture, though some auxiliary blowing agents are also usually utilized (Herrington and Hock, 1998).

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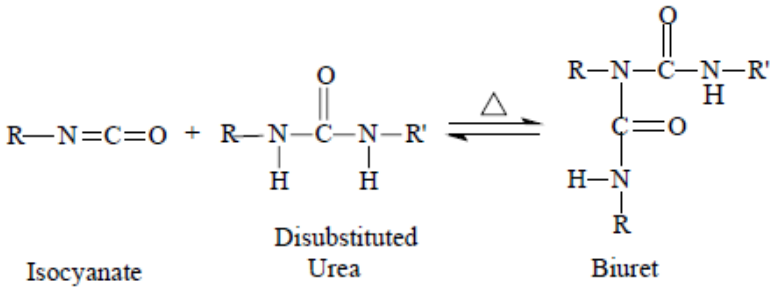
1.2

There are other secondary reactions involving the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking points. In the formation of biuret, a hydrogen atom from the disubstituted urea reacts with an isocyanate group to form a biuret linkage, as shown in Equation 4(Herrington and Hock, 1998).



1.3

Isocyanate Amine Disubstituted Urea

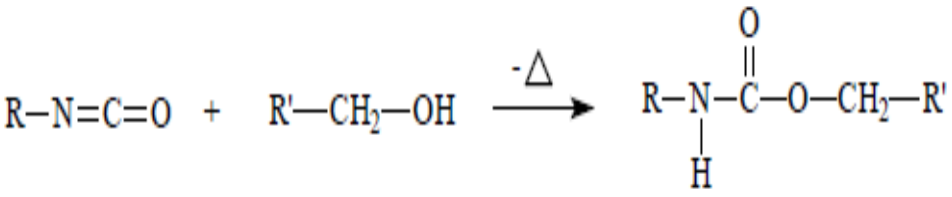


1.4

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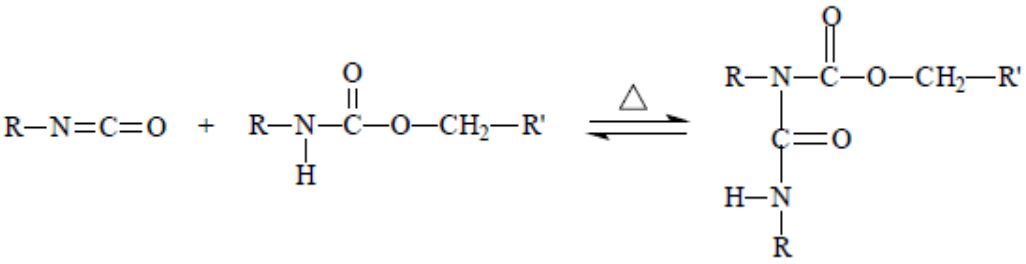
2.4.1.2 Gelation Reaction

The gelation reaction, sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in Equation 5. The heat of this reaction is reported to be approximately 24 kcal per mole of urethane formed (Herrington and Hock, 1998). Since polyurethane foams usually utilize polyfunctional reactants (typically di-functional isocyanates and tri-functional polyols), this reaction leads to the formation of a cross-linked polymer. The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer as shown in Equation 6 In uncatalyzed systems, this reaction is known to be insignificant (Herrington and Hock, 1998).



1.5

Isocyanate Alcohol Urethane



1.6

IsocyanateUrethane Allophanate

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The gelation reaction covalently bonds these urea hard segments to form soft polyol segments. When the concentration of the hard segments exceeds a system dependent solubility limit, the hard segments phase separate out and form what is commonly referred to as ‘urea microdomains (Herrington and Hock, 1998). In addition, at higher water contents (and thus at higher hard segment contents), the urea microdomains are known to aggregate and form larger urea rich structures commonly termed ‘urea balls’ or ‘urea aggregates’. These urea balls are regions richer in urea compared to the general surrounding polyol matrix which also contains dispersed urea microdomains. A schematic representation of this phase-separated morphology is provided in Figure 2.1.

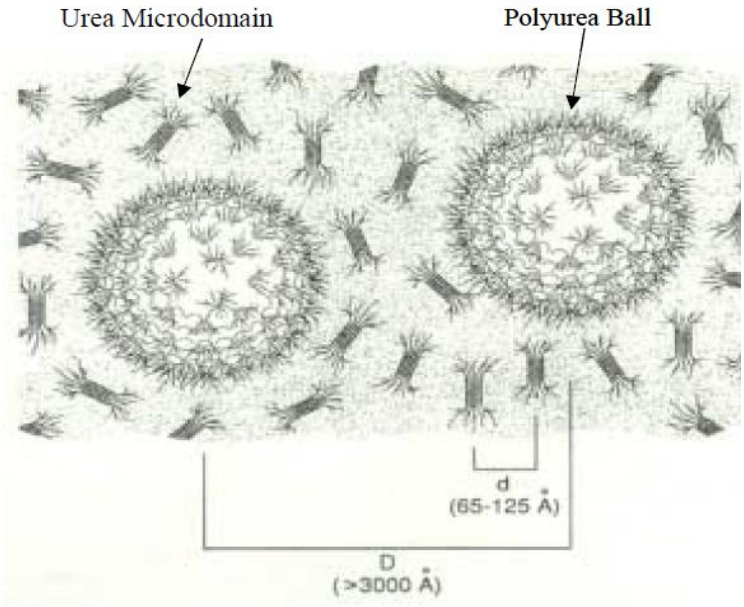


Figure 2.1: Schematic Representation of the Phase Separation Behavior in Polyurethane Foams(Kaushiva and Wilkes, 2000).

2.4.2 Basic Foam Components

There are many different components needed to synthesize flexible foam. The seven major ones are isocyanate, polyol, water, physical blowing agents, catalyst, surfactants, and cross-linking

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agents (Kaushiva and Wilkes, 2000). The desired end properties of the foam dictate the choice of specific components along with their required quantities (Armistead, 1985). Each application of flexible polyurethane foams has specific performance criteria, sothere are many components needed in a typical formulation to ensure that the product will beopen-celled and still meet other requirements as shown in Table 2.2. (Kaushiva and Wilkes, 2000).

Table 2.2 Formulation Basics for Flexible Polyurethane Foams (Kaushiva and Wilkes, 2000).

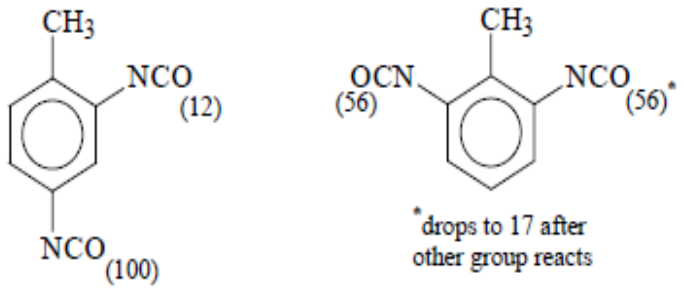
Component	Parts by Weight Polyol
Polyol	100
Inorganic Fillers	0-150
Water	1.5-7.5
Silicon Copolymer Surfactant	0.5-2.5
Amine Catalyst	0.1-1.0
Tin Catalyst	0.0-0.5
Chain-Extender	0-10
Cross-Linker	0-5
Additives	Variable
Auxiliary Blowing Agent	0-35
Isocyanate	25-85

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2.4.2.1 Isocyanates

The two most common sources of isocyanate functionalities in foam production come from toluene diisocyanate (TDI) and di-phenylmethanediisocyanate (MDI), of which the former is more commonly used in North America, and the latter one has a greater market demand in Europe. TDI exists in two isomeric forms, both of which are used in foam production. The two isomers differ mainly in two ways. Firstly, as indicated in Structure 2.1, the relative reaction rates of the different isocyanate groups on each molecule differ considerably (Herrington and Hock, 1998).

The reactivity of the *ortho*position in the 2,4 isomer is approximately 12% of the reactivity of the *para* position due to the steric hindrance caused by the methyl group. However, when the reaction temperature approaches 100°C, steric hindrance effects are overcome and both the positions react at nearly the same rate. In comparison, the NCO groups on 2,6 TDI have equal reactivity though the reactivity of the second isocyanate group drops by a factor of around 3 after the first group reacts (Herrington and Hock, 1998).



2,4 TDI 2,6 TDI

Structure 2.1: Isomers of Toluene Diisocyanate(Herrington and Hock, 1998).

Depending on the pathway chosen between these two steps, three industrially common mixtures of the two isomers of TDI can be generated – 65:35 2, 4/2,6 TDI (TDI-65), 80:20 2,4/2,6 TDI

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(TDI-80), and 100% 2,4 TDI (TDI-100). Of these mixtures, the 80:20 blend is, by volume, the most important (Kaushiva, 1999). Several issues with regard to the isocyanate have been addressed and are available in the literature(Fuad *et. al.*, 1995), presented the challenges which MDI-based foams face over conventional TDI foams (Fuad*et al*, 1995).

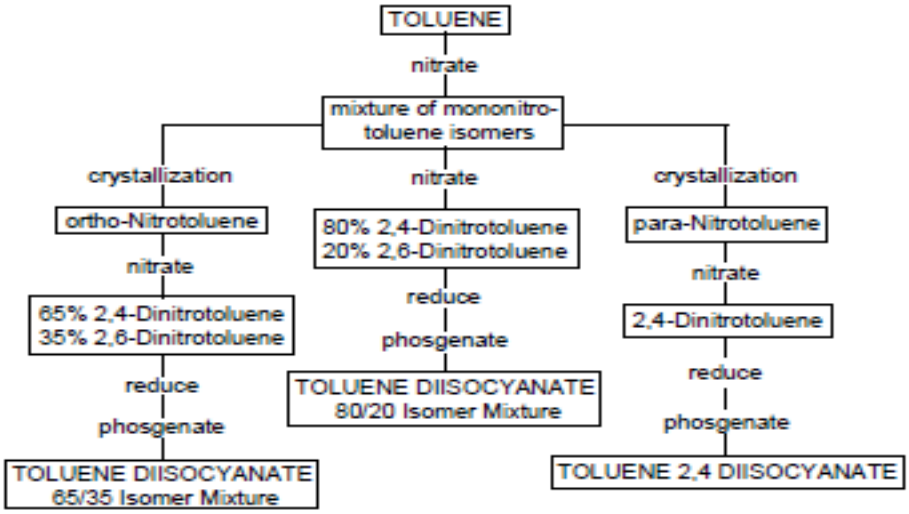


Figure 2.2: Routes for the Production of Commercial TDI Blends(Herrington and Hock, 1998).

2.4.2.2 Polyol

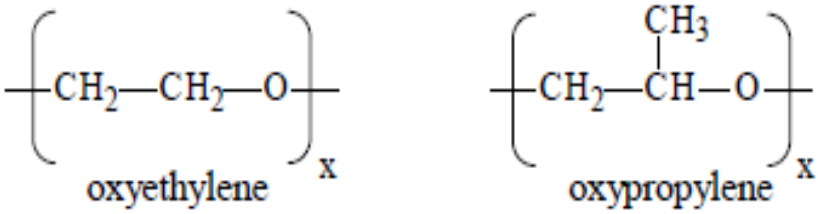
The polyol forms the backbone of the polymer chain since it serves as the source of the hydroxyl for the isocyanate which determines the hardness of the foam(Babalola and Dominic, 2012). The soft phase of polyurethane foam is usually a polyfunctional alcohol or polyol phase which on reacting with isocyanate groups covalently bonds with urea hard segments through urethane linkages (Kaushiva and Wilkes, 2000). Glycols such as ethylene glycol, 1,4-butanediol, and 1,6-hexanediol are relatively much lower in molecular weight compared to the polyols used in flexible foam production.

These are more commonly used for chain extension to form hard segments in polyurethane elastomers and therefore will be referred to as ‘chain extenders’. Polyols used for flexible foam formulations are higher molecular weight (approximately, 3000 to 6000 g/mol) and have average

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functionalities in the range of 2.5 – 3.1. Polymerization processes allow production of a wide range of polyols, differing in molecular weight, functionality, reactivity, and chain structure(Dounis et al., 1993). There are two kinds of polyols commercially available for flexible foam production, hydroxyl terminated polyethers and hydroxyl terminated polyesters (Makanjuola, 1999).

Furthermore, the polyether polyols are produced by ring opening propoxylation or ethoxylation onto a variety of starting materials called initiators. About 90 % of the flexible polyurethane foam market utilizes polyether polyols based on propylene oxide in comparison to polyester polyols, because of their lower cost, better hydrolysis resistance, and greater ease to handle (Kaushiva and Wilkes, 2000). The common polyether polyols used in flexible foam production utilize ethylene oxide (EO) and propylene oxide (PO) as the repeat units (Structure 2.2). The polyols produced are typically random hetero fed copolymers of EO and PO, though in some cases where high reactivity of the polyol is required, the polyol is EO end-capped. This is because primary hydroxyl groups are approximately three times more reactive towards isocyanates as compared to secondary hydroxyl group, Herrington and Hock (1998).



Structure 2.2: Repeat Units of the Common Polyether Polyols used in Flexible Foam Production(Herrington and Hock, 1998).

Early research work has focused on producing elastomers and rigid foams from entirely natural polyols which were proven to be successful. However, challenges remain in making flexible

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foams, the most significant polyurethane product, using entirely natural polyol (Kaushiva and Wilkes, 2000).

2.4.2.3 Water

Water acts as a chemical blowing agent and reacts with an isocyanate group resulting in a primary amine and carbon dioxide. Increasing the water content influences both the cell structure and the solid-state morphology of the foam (Kaushiva and Wilkes, 2000). Higher water content typically result in foams with lower density due to the increased blow reaction, as seen in Figure 2.1(Kaushiva and Wilkes, 2000). Also, since the hard segment content is also increased when more water reacts with the isocyanate, this increases the stiffness of the polymer composing the foam struts.

However, Kaushiva and Wilkes (2000) observed that increasing the water content while maintaining other variables constant does not drastically affect the load bearing properties of the foam. For example, the hardness of the foams corresponding to curve A in Figure 2.3 have been reported to be in the range of 250-350 N as the water content is varied from 2.0 to 5.0 pphp. This according to Harrington and Hock (1998), is due to the fact that the two opposing factors discussed above compensate each other, and by and large, the load bearing properties remain unchanged.

2.4.2.4 Physical Blowing Agents

Water and methylene chloride- These, being sources of active hydrogen, react with isocyanide to produce carbon dioxide which causes the foam cells to rise (Babalola and Dominic, 2012). Although the carbon dioxide produced from the water-isocyanate reaction acts as the principal source to blow the foam, some formulations also employ physical or auxiliary blowing agents. These are low boiling solvents, inert towards chemical reactions, and are generally used to

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produce softer foams by reducing the foam density (Kaushiva and Wilkes, 2000). As the foaming reactions proceed, the temperature reaches approximately, 130 ^{o}C, and this is high enough to vapourize the low boiling solvents and provide supplementary gas to expand the foam. Addition of a physical (auxiliary) blowing agent while maintaining the water/isocyanate content typically results in larger cells and greater degree of cell openness, which results in a decreased foam density generally leading to increase in foam softness (Herrington and Hock, 1998; Kaushiva and Wilkes, 2000).

Until the early 1990's, the auxiliary blowing agent primarily used to produce soft low-density foams was chlorofluorocarbon CFC-11 (CFCl3)(Kaushiva and Wilkes, 2000). This blowing agent was, however, phased out in 1995 due to the environmental concern it caused regarding the depletion of the ozone layer, especially over Antarctica (Douni*et al.,* 1993). Other alternatives involving the use of acetone19 and liquid carbon dioxide have been suggested in the literature (Eiben*et al.,* 1995). Blowing agents such as pentane have been tried to replace CFCs although they are less satisfactory and also raise flammability concerns.

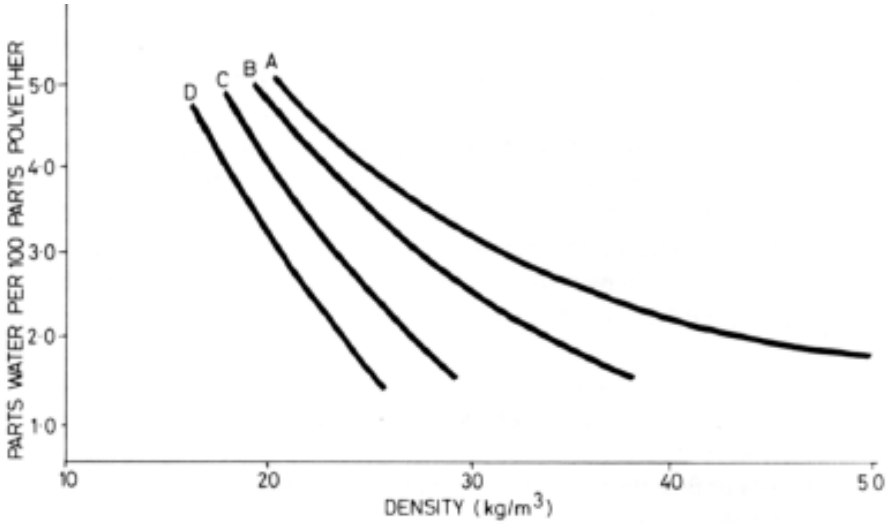


Figure 2.3: Slabstock Polyether Foams water/CFC-11/density/ hardness relationship (Kaushiva and Wilkes, 2000).

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2.4.2.5 Catalysts

The catalysts are organo-metallic compounds and the commonest one is stannous octoate. Stannous octoate, amine and silicone - Stannous octoate is an organic-metallic catalyst for the reaction between the polyol and the isocyanate while the amine catalyzes the reaction between water and the isocyanate. Silicone, however, is a surfactant which lowers the bulk surface tension of the reacting mixture and stabilizes the foam bubbles formed (Babalola and Dominic, 2012). In the formation of polyurethane foams, the catalyst forms an activated complex with the reactants thus making it easier for the isocyanate moieties to chemically react with the active hydrogen containing compounds (Herrington and Hock, 1998; Kaushiva and Wilkes, 2000).

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Table 2.3: The Reactivity of Isocyanates with Active Hydrogen Compounds (Herrington and Hock, 1998).

Active Hydrogen Compound	Typical Structure	Relative Reaction Rate (Uncatalyzed At 25^{o}c)
Primary Alliphatic Amine	RNH_2	100,000
Secondary Alliphatic Amine	R_2NH	20,000-50,000
Primary Aromatic Amine	$ArNH_2$	200-300
Primary Hydroxyl	RCH2OH	100
Water	H_2O	100
Carboxylic Acid	RCOOH	40
Secondary Hydroxyl	R_2CHOH	30
Urea	RNHCONHR	15
Tertiary Hydroxyl	R_3COH	0.5
Urethane	RNHCOOR	0.3
Amide	$RCONH_2$	0.1

Since polyurethane foam production relies on two competing reactions, a balance between them is required to make foams with good open-celled structures and desired physical properties. While it is true that these reactions may proceed in the absence of catalysts, they generally proceed at rates too slow to be practical (Kaushiva and Wilkes, 2000). Catalyzing polyurethane

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foam formation, therefore, involves choosing a catalyst package in such a way that the gas produced becomes sufficiently entrapped in the polymer. The reacting polymer, in turn, must have sufficient strength throughout the foaming processto maintain its structural integrity without collapse, shrinkage, or splitting (Kaushiva and Wilkes, 2000).

2.4.2.6 Surfactants

Flexible polyurethane foam production relies greatly on the performance of non-ionic, silicone based surfactants which are added to realize a variety of functions. In fact, the largest commercial application of silicone surfactants is in the area of polyurethane foams with worldwide production quantities of 30,000 metric tons/year for the polyurethane foam industry (Reed, 1995). Some of the main functions performed are reducing surface tension, emulsifying incompatible ingredients, promoting bubble nucleation during mixing, stabilization of the cell walls during foam expansion, and reducing the de-foaming effect of any solids added. The processing window for surfactants is generally in the range of 0.5-2.5 parts per hundred polyol (pphp), and the actual quantity of surfactant added is dependent on the type of surfactant used as well as on the other constituents of the foam formulation (Kaushiva and Wilkes, 2000).Below a certain minimum concentration of surfactant, the foam can result in serious imperfections, such as splitting, densification, or collapse. At high levels of closed windows, this lack of airflow can induce the foam to shrink as it cools. These ideas are summarized in Figure 2.4 where airflow through a 1" thick foam sample is plotted versus surfactant concentration (Kaushiva and Wilkes, 2000; Herrington and Hock, 1998).

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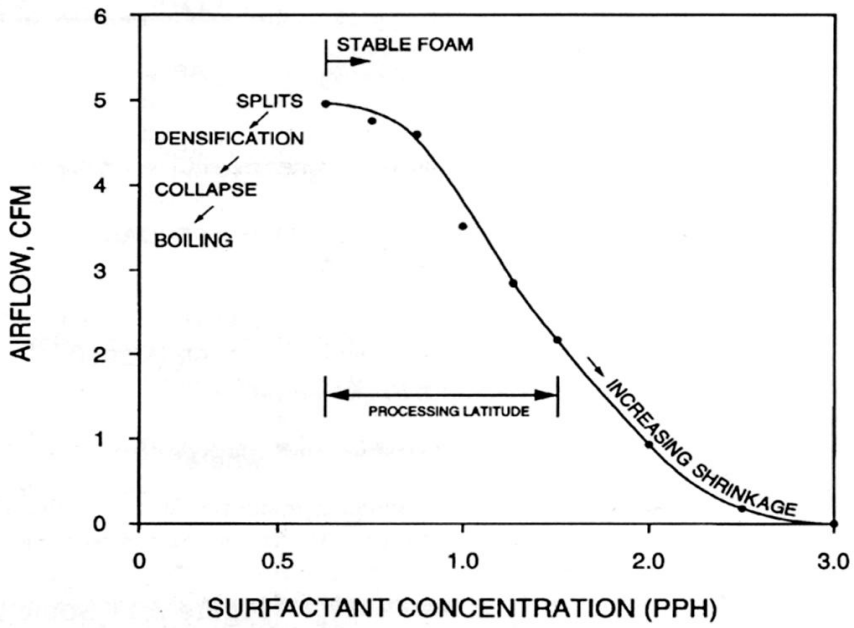


Figure 2.4: Effect of Surfactant Concentration on FoamStability (Herrington and Hock, 1998).

Table 2.4: Molecular Weights and Copolymer Compositions of Silicone Surfactants Used for Flexible Polyurethane Foams (Chen *et al.*, 2001).

Application	Surfactant Molecular Weight	Weight Percent Silicon	Polyether Molecular Weight	Weight Percent E.O in Polyether
Molded	300-1,500	30-100	0-800	0-100
Slabstock	03,000-80,000	15-30	1,000-4,000	35-65

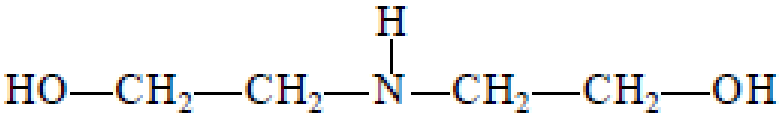
2.4.2.7 Cross-linking Agents

Cross-linking agents in flexible polyurethane foams are usually low molecular weight species with hydroxyl and/or amine groups and have functionalities greater than or equal to 3. The

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example shown in Structure 2 is diethanol amine (abbreviated as DEOA), a commercially utilized cross-linker, which is commonly used in molded foam applications as it helps in a faster viscosity build-up and thus in achieving shorter demold times.

Also, since molded foam applications utilize high molecular weight polyols and slightly higher catalyst doses compared to slabstock formulations, using typical foam surfactant leads to an over-stabilization of the cell walls. Thus, lower potency surfactants are utilized in molded-foams, to counteract this over-stabilization effect (Kaushiva and Wilkes, 2000). A systematic study initiated by Dounis and Wilkes and continued by Kaushiva and Wilkes (2000) using DEOA as a cross-linking agent revealed that the hard segment ordering was lost on addition of DEOA, thus leading to the observed softening of the foam (Dounis and Wilkes, 1997; Kaushiva and Wilkes, 2000).



Structure 2.3: Diethanolamine (DEOA) (Dounis and Wilkes 1997).

2.4.2.8 Other Additives

Fillers, colorant and flame retardants – Fillers increase density, colorants give the desired colour and flame retardants inhibit ignition which is a serious hazard posed by the highly exothermic reaction between water and the isocyanate (Babalola and Dominic, 2012).Various additives are added to flexible polyurethane foam formulations depending on the required properties and the end use of the foam. Some additives are added for aesthetic reasons (for example colorant), others are added to improve product performance. Since polyurethane foams have a significant amount of aromatic content, UV stabilizers are added toretard the yellowing of foams on

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exposure to light (Herrington and Hock, 1998). Some other additives include the use of non-reactive plasticizers to reduce viscosity, cell-openers to prevent shrinkage of the foam on cooling, and compatibilzers to enhance the emulsification of the reactants (Herrington and Hock, 1998).

2.5 The Foaming Process

Fourier transform infra-red spectroscopy (FTIR) has been extensively used to study the sequence of the foaming reactions. In general, there is agreement amongst different workers that the water-isocyanate reaction takes place sooner and faster as compared to the polyol-isocyanate reaction (Kaushiva and Wilkes, 2000). This is supported by growing urea carbonyl absorption at ca. 1715 cm^{-1} early in the reaction which is observed to shift to ca. 1640 cm^{-1} once half the foam rise height is reached. Model studies carried out on diphenyl urea have indicated that the urea carbonyl absorption in a good solvent (DMF) and a poor solvent (THF) appears at 1715 and 1640 cm^{-1},respectively (Mothe et al., 2002). The urethane formation, however, were not significant in the first 5-10 min, but was found to increase at a steady rate for the next 30 min. These results were also confirmed by Rossmy and co-workers who observed that the ratio of isocyanate to water consumption was 2:1 in the early part of the foam reaction, indirectly indicating that urethane formation was not significant in earlier stages (Mc Cabe et *al.,* 1993).

2.6 Morphology

The physical properties of flexible polyurethane foams are a function of both the cellular structure and the phase separated morphology of the polymer comprising the struts of the foam (Herrington and Hock, 1998). These two factors are intimately related because both are

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influenced by the forces exerted during the expansion and stabilization of the foam. There has been considerable effort to try and understand how these two factors influence the physical properties of the foam such as load bearing, compressive stress-relaxation, creep, and also how these properties are a function of varied temperature and humidity conditions (Herrington and Hock, 1998).

While testing polyurethane foams, it is often found difficult to separate the effects of cellular structure and the solid state polymer morphology on the foam properties (Armistead, 1985).

2.6.1 Cellular Structure

The properties of flexible polyurethane foams are a strong function of its cellular structure. A complete knowledge of the cellular structure of foam would require the exact size, shape, and location of each cell (Dounis and Wilkes, 1997). Earlier researchers described the shape of the foam cells similar to that of a pentagonal dodecahedron, which has twelve five-sided faces as shown in Plate 2.1 (Kaushiva and Wilkes, 2000).

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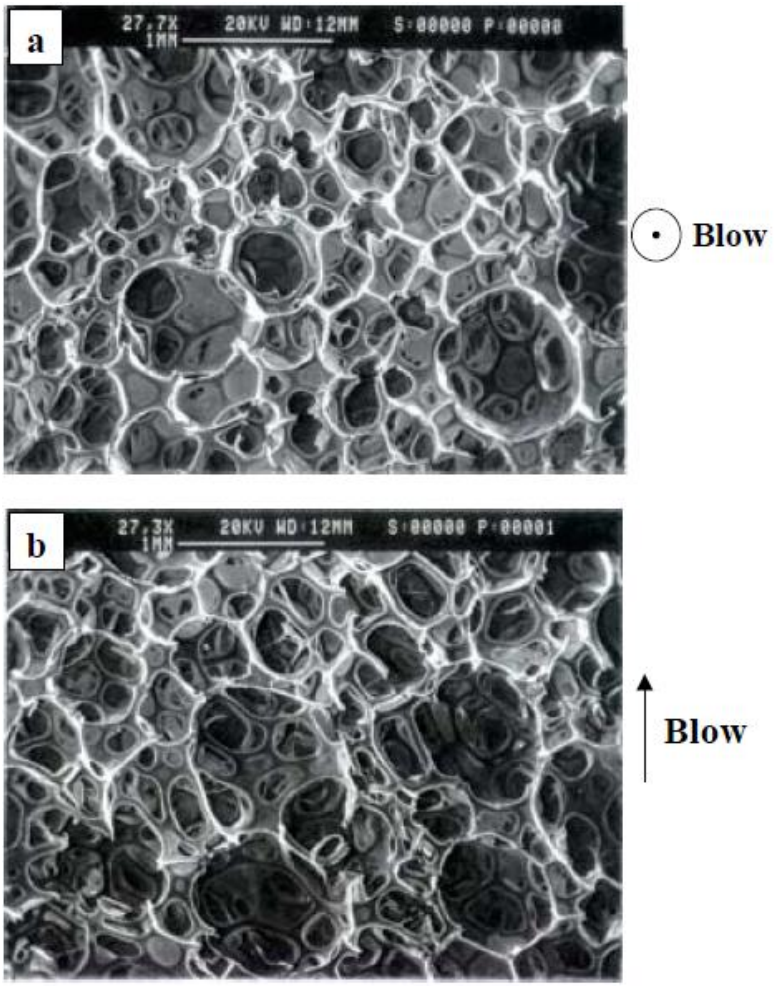


Plate 2.1: Typical SEM Micrographs of Conventional Molded Polyurethane Foam. (a)Parallel to the rise direction (b) Perpendicular to the rise direction (Armistead, 1985).

2.6.2 Polymer Morphology

The cellular structure observed in flexible polyurethane foam plays important role in determining its physical properties. If not greater, of equal importance is the morphology of the polymer which comprises the solid portion of the foam. Over the years, workers have utilized several techniques to investigate this solid state morphology. Until the early 1980's Infrared Radiation (IR) spectroscopy was the primary characterization technique.

The last 20 years, however, have seen the application of Small angle X-ray scattering (SAXS), Wide-angle X-ray scattering (WAXS), Transmission electron micrograph (TEM); (Herrington

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and Hock, 1998; Armistead, 1985; Dounis and Wilkes, 1997; Kaushiva and Wilkes, 2000; Dounis and Wilkes, 1999), and more recently Atomic force microscopy (AFM) (Kaushiva and Wilkes, 2000).

2.6.2.1 Urea Micro-domain Considerations

The isocyanate-water reaction proceeds faster as compared to the reaction between the isocyanate and the polyol. This leads to the formation of oligomeric poly-urea, species which are termed as urea hard segments. When the molecular weight of these urea hard segments exceeds a system dependent solubility limit, thermodynamic boundaries are surpassed, resulting in a transition from an initial inhomogeneous disordered state to an ordered micro-phase separated state (Armistead *et al.,* 1988).The characteristic properties of flexible polyurethane foams depend much less on the covalent cross-linking points present in the polyol phase and more on the cohesive strength of the microphase separated urea hard domains, which provide physical cross-linking points (Herrington and Hock, 1998).

However, the morphology of these systems should not be oversimplified. There exists in some of these foams another structure which is less well understood. At high enough water concentration for a specific polyol system (with stoichiometric isocyanate feeds), aggregations of polyurea may form which are much larger than the microdomains. Whereas the microdomains are approximately 30-60 Å in size with interdomain spacings of approximately 70-120 Å, these macrodomains are more spherical and ca. 3000 Å in diameter. This morphology is schematically represented in Plate 2.1, and its water concentration dependence can be seen in the TEM micrographs of Plate 2.2.

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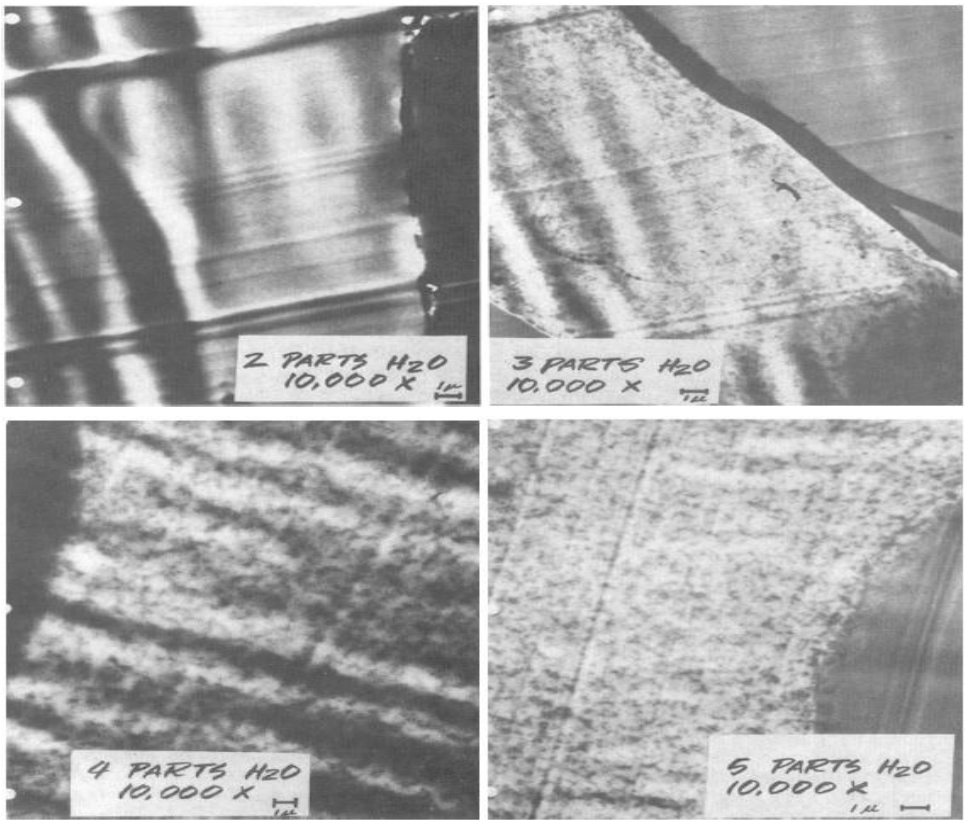
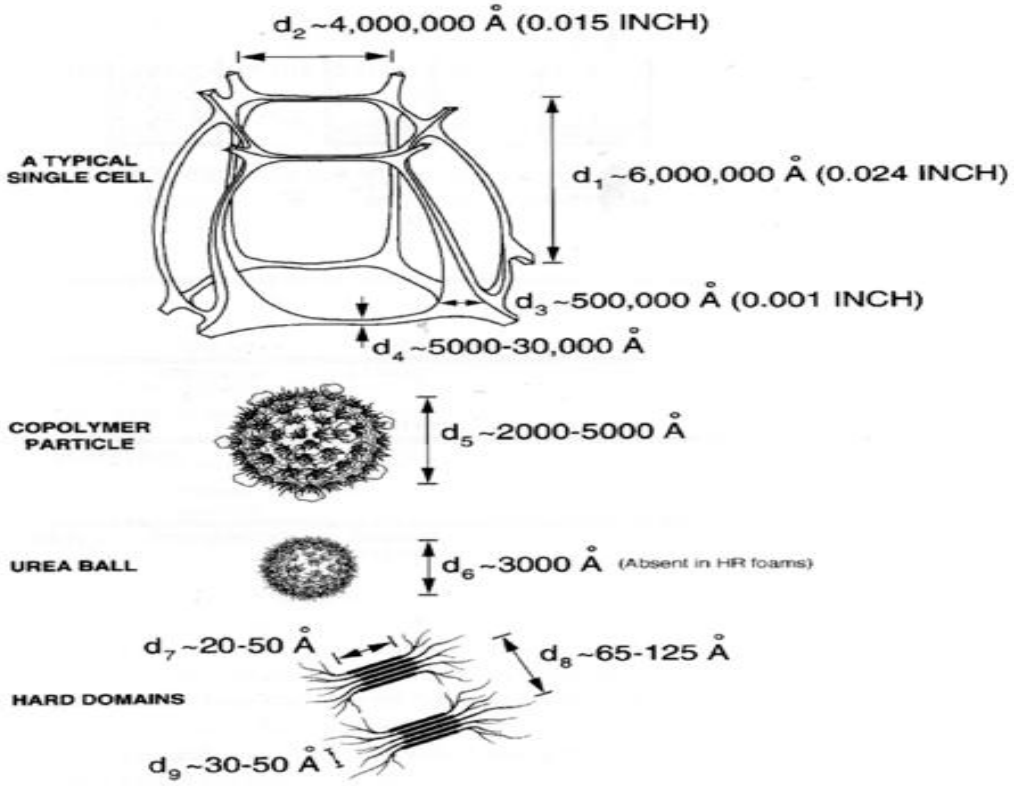


Plate 2.2: TEM micrographs of slabstock foams varying in water content (Armistead, 1985).

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Structure 2.4: Simplified Model for the Morphological Features Found in Flexible Polyurethane Foams (Kaushiva et al., 2000).

2.7 Properties which affect Foam Performance

There are a number of physical properties of flexible polyurethane foam that can be used when selecting foam for different applications. The following is a brief description of the physical properties of foam, and the importance of each.

2.7.1 Density

Density is a measurement of the mass per unit volume. Measured and expressed in pounds per cubic foot or kilograms per cubic meter. Density is one of the most important of all foam properties. Density affects foam durability and support. Typically, the higher the polymer

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density, the better the foam will retain its original properties and provide the support and comfort it was originally designed to produce (Umar, 2010).

2.7.2 Indentation Force Deflection(IFD)

Indentation Force Deflection (IFD) is a measurement of foam firmness. Firmness is independent of foam density, although it is often thought that higher density foams are firmer. It is possible to have high density foams that are soft-or low density foams that are firm, depending on the IFD specification. It is measured by indenting the foam 25% of its original height (Umar, 2010).

2.7.3 Support Factors

A second IFD measurement is sometimes taken by indenting the foam 65 percent of its original height. This second IFD measurement is used to help determine the ability of the foam to provide deep down support. Typically, the more difference between the 25 % IFD and the 65 % IFD, the more ability the foam has to support weight. The ratio of the 65 % IFD divided by the 25 % IFD is called the foam's support factor. Support factors for foam range from about 1.5 to 2.6. Typically, the higher the foam density, the better the support factor (Umar, 2010).

2.4.4 Flex Fatigue(Dynamic Fatigue)

There are several tests that are used to determine foam durability, or how well foam retains its original firmness properties and height. Some are standard laboratory tests; others are customized tests developed by different manufacturers. But virtually all of them are based on flexing or compressing the foam a specific number of times and measuring foam firmness and height before and after testing. In flex fatigue testing, foam samples may be compressed a few thousand times, or many thousands of times. Shorter tests provide an idea of how much firmness a foam may lose through initial use, while longer tests provide data on overall foam durability(Umar, 2010).

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2.7.5 Roller Shear

A particularly severe flex fatigue test is roller shear, where a rolling weight is run over a foam sample from two directions, typically for about 25,000 cycles. This test provides a combination of compression and abrasion, and helps identify how the foam would stand up to particularly difficult applications, such as commercial furnishings or as carpet cushion. Again, IFD loss is measured, and multiple measurements may be taken, at different time periods after the foam has had a chance to "recover" (Umar, 2010).

2.7.6 Tear Strength

Flexible polyurethane foams ability to resist tearing or shredding can be measured by their tear strength. The tests to determine these properties are tensile strength tear resistance, and elongation. They determine the foam's ability to be stretched or flexed without tearing. These durability measurements are particularly important for foams which contain large amounts of fillers, such as combustion modified foams. These additives can increase the tendency of foams to tear or shred. When specifying foams which contain additives, it is suggested that tensile strength, tear and elongation tests be reviewed to see if the foam may require special handling (Umar, 2010).

2.4.7 Resilience

Resilience is an indicator of the surface elasticity or "springiness" of foam. Resilience can relate to comfort. Resilience is typically measured by dropping a steel ball onto the foam cushion and measuring how high the ball rebounds. Foam resilience ranges from about 40 % ball rebound to as high as 70 %t rebound. Higher resilience in foam often means thatsofas, seat or cushions for example, have a better "hand" or surface feel (Umar, 2010).

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2.7.8 Combustibility

When selecting a polyurethane foam or a product containing polyurethane foam, consideration should be given to the anticipated ultimate end use of the foam or product, the type of occupancy or vehicle in which its use is anticipated, the flammability characteristics of available polyurethane foams, and the fact that burning polyurethane foam emits toxic gaseous products. Foam is an organic material and is combustible like all organic materials. Organic materials include a wide range of substances like wood, wool, paper, cotton, nylon, polyester, and polyethylene.

Polyurethane foam, once ignited, can burn rapidly, consuming oxygen at a high rate and generating great heat. Polyurethane foam should not be exposed to open flames or other direct or indirect high-temperature ignition sources such as burning cigarettes, matches, fireplaces, space heaters, or naked lights. Like any other organic material, when it is ignited and burns, polyurethane foam liberates smoke containing toxic gases, the primary one being carbon monoxide (Amstead*et al.,* 2010).

2.8 Fillers

Fillers are finely divided inorganic compounds are purposefully added to foam formulations in order to increase their density, load-bearing ability and sound attenuation capacity at the expense of some undesired physical properties as well as some desired properties but to a safe degree. Also, depending on the nature of the filler used, significant cost reduction can be achieved (Onuegbu*et al.,*2010). Fillers used in foam formulations can be inorganic in nature, but it is difficult to produce a stable suspension, and for this reason, organic fillers are usually preferred

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(Isaac *et al.*, 2012).Fillers capable of enhancing strength properties of a polymer are said to be reinforcing (Onuegbu*et al.*,2010).

However, the effect of fillers on the properties of the foam depends on factors such as surface area, porosity, bulkiness and surface chemistry. The use of filler to modify properties of composition can be traced to at least as far back as in the middle of the 19th century in Roman era when artisans used ground marble, calcium carbonate ($CaCO_3$) in lime plaster, frescoes and pozzolanic mortar, paper and paper coating (Onuegbu*et al.*, 2010). Functional fillers were developed on a commercial scale in the early 20th century when carbon black was added to rubber and phenol-formaldehyde plastics were formulated with wood floor.

Different types of fillers are employed in resin formulations; the most common are calcium carbonate, talc, silica, wollastonite, clay, calcium sulfate, mica, glass structures, and alumina trihydrate. Fillers serve a number of purposes. Inert materials like wood flour, clay, and talc serve to reduce resin costs and, to a certain extent, improve processability and heat dissipation in thermosetting resins. Both alumina trihydrate and talc improve flame retardance. Mica is used to modify the electrical and heat-insulating properties of a polymer. Parts molded from composites containing phlogopite mica as a reinforcement exhibit little or no warpage on demolding or subjection to elevated temperature. A variety of fillers, e.g., particulate fillers like carbon black, aluminum flakes, and metal or metal-coated fibers may be used to reduce mold shrinkage as well as to produce statically conductive polymers, shielding of electromagnetic interference/radio frequency interference (EMI/FMI) (Umar, 2010). Particulate fillers such as carbon black or silica are used as reinforcing fillers to improve the strength and abrasion resistance of commercial elastomers (Isaac et al., 2012). Fibers such as asbestos, glass, carbon, cellulosics, and aramid are used principally to improve some mechanical property/properties such as modulus, tensile

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strength, tear strength, abrasion resistance, notched impact strength, and fatigue strength as well as enhance the heat-deflection temperature (Toro et al.,, 2007).

Historically, inorganic fillers such as barium sulfate and calcium carbonate have been used in flexible slabstock foams to achieve increased density and/or load bearing, and to reduce cost. Normal used concentrations range from 20 to 150 parts per hundred parts polyols (Babalola and Dominic, 2012). The use of inorganic fillers has several disadvantages including: difficulty of preparing and maintaining the dispersion; problems with removal of entrained air; difficulty of mixing and pumping the filler/polyol slurry; loss of the foam physical properties; difficulty of processing on all types of foam machinery, and, due to their abrasive nature, increased wear on machinery components (Umar, 2010).

Table 2.5: Fillers and Their Applications in Polyurethane Foams(Umar, 2010).

Filler	Typical Applications
Calcium carbonate (ground chalk, ground limestone, whiting)	Flexible foams, semi rigid foams, binder compositions, rigid integral skin foams.
Barium sulphate (barytes)	Flexible foams, semi rigid foams, especially for sound absorption.
Clays (china clay, kaolins, etc)	Flexible systems.
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers.
Clay balls, vermiculite	Rigid foams..
Silicates, cements	Rigid foams, sealants, grouting.
Glass cloths and scrims, wire mesh, organic fibers	Encapsulation in rigid foams, reinforcement of low-density flexible foam moldings.

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Mineral fillers are also used to reduce costs, and to increase the compressive strength of rigid foams used in composite building panels. Finely divided fillers with particle size ranging from a few microns up to about 100 microns are usually added as dispersers in the polyol component of the PU systems (Niemiyer *et al,* 2006), some low cost mineral fillers such as China clay, kaolins, and other aluminium silicates, which contain both free and combined water, which would otherwise be satisfactory, may be difficult to dry reproducibly and economically (Umar, 2010). Care must be taken to dry the fillers or to know the precise water content available and factor that data into the foam calculations.

Also, fibrous fillers are reinforcers: they give increased stiffness and the operating temperatures of rigid foams, integral and flexible RIM products. The degree of reinforcement obtainable depends on the strength of the fiber, the concentration, the modulus and extensibility of the polymer matrix, the interfacial adhesion and the shear strength at the fiber/polymer interface, and on the orientation of the fibers (Bledzi and Faruk, 2006). Different kinds of fillers and thier respective applicationsin polyurethane form was summerised in Table 2.5 above.

2.8.2 The Effect of Fillers

Filler as used in plastics and rubber industries is a finely divided solid material which is added to the liquid, semi liquid or solid composition to modify the physical properties of the composite and to reduce cost (Onuegbu*et al.*,2010).

However, the effect of fillers on the properties of the foam depends on factors such as surface area, porosity, bulkiness and surface chemistry. The use of filler to modify properties of composition can be traced at least as far back as in the middle of the 19th century in Roman era

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when artisans used ground marble, calcium carbonate($CaCO_3$) in lime plaster, frescoes and pozzolanic mortar, paper and paper coating (Kirk-Othmer, 1998).

Functional fillers were developed on a commercial scale in the early 20th century when carbon black was added to rubber and phenol-formaldehyde plastics were formulated with wood floor. Fillers can be organic such as wood floor, paper pulp, carbon black; eggshell etc or inorganic which includes asbestos, powdered mica, talc and lead oxide (Babalola and Dominic, 2012).

2.9 Eggshell

An eggshell is the outer covering of a hard-shelled egg and of some forms of eggs with soft outer coats (Abdullah *et al.*, 2011). The composition of eggshell is approximately 98.2, 0.9, 0.9% calcium carbonate, magnesium and phosphorous (phosphate) respectively (King'ori, 2011). Eggshell is a natural bio-ceramic composite with a unique chemical composition consist of high inorganic content (~ 95% of calcium carbonate) and ~5% of organic components (Iyer and Torkelson, 2014). The mechanical properties of the eggshells are influenced by the interaction between these organic and inorganic constituents (Iyer and Torkelson, 2014). The distinctive structure of eggshell combined with the substantial availability makes eggshells a potential source of bio-fillers that can be efficiently used for polymer nano-composites.

Chicken eggshell (ES) is an agricultural byproduct that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the U.S. alone, about 150,000 tons of this material is disposed in landfills (Ishikawa *et al.,* 2004). However, report we have shown, among other characteristics that ES has a relatively lower density compared to mineral calcium carbonate (Abdullah et al., 2011).Egg shell structure, which varies widely among species, is a protein lined with mineral crystals,

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usually of a calcium compound such as calcium carbonate These characteristics qualify ES as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories.

2.9.1 Eggshell production in Nigeria

The projected population of poultry in Nigeria as presented by the Federal Department of Livestock and Pest Control Services puts the estimated population of poultry in Nigeria as at year 2003 as 137,678,943 comprising 115,880,864 or 84% as backyard poultry and 21,798,079 or 16% as exotic poultry (Amu *et al.,* 2005). The annual production capacity of the commercial poultry in Nigeria is estimated as 96,981,001kg dressed broilers, 40,738,698kg dressed culled layers and 8,216,208,000 eggs (273,873,600 crates of eggs), and the estimated annual egg production is 8,216,208,000 eggs, as reported by the Food and Agriculture Organization (F.A.O) of the United Nations, 2008. The food industry in Nigeria uses large quantities of eggs, so eggshell disposal poses a significant challenge to the industry in these times of increasing awareness of environmental safety.

Researchers have reported the use of eggshells as a reinforcement material in polymer matrices. Toro *et al.,* (2007) used different weight fractions of chicken eggshell as bio-filler to improve the properties of polypropylene. The average size of the eggshell particles was approximately 8.4 μm and the surface area was approximately $18m^2/g$ Toro *et al.,* (2007). The mechanical properties of eggshell/polypropylene composite showed significant improvements compared to other polypropylene composites reinforced with commercial talc and calcium carbonate fillers.

Furthermore, eggshell/polypropylene composites demonstrated better eggshell/matrix interface. The formed polypropylene composite contained eggshell reinforcements with weight fractions varied from 20 to 60% (Toro *et. al.,* 2007). Iyer*et al.,* (2014) developed eggshell/polypropylene

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composites with improved mechanical and thermal properties compared to polypropylene composite reinforced by traditional mineral particles (Arias *et. al.*, 2008). Ji and coworkers also reported substantial improvements in the mechanical performance of di-glycidyletherbisphenol A epoxy resin infused with 5 wt% of chicken eggshell micro-particles (average particles size 9.36μm and 17.4m^2/g surface area) (Ji*et al.*, 2009). Xu and Hanna studied the infusion of 2%, 6% and 10% by weight of eggshell particles in a composite foam material derived from corn starch for food packaging application. The as-prepared composites exhibited enhanced thermal and mechanical properties due to the infusion of micron size eggshell particles (Xu and Hanna, 2007).

However, the dispersion of additives and fillers in the polymer matrix is one of the important aspects of polymer processing. The degree with which the nano-particles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal and mechanical properties of the material. Poor dispersion can lead to diminution of the properties in the resulting material. Researchers have reported a number of nano-particles dispersion methods include (1) mechanical agitation, such as ball milling or magnetic stirring, (2) ultrasonic vibration, (3) shear mixing, (4) non-contact mixing, and (5) using the dispersing agent (Toro et al., 2007).

Again, finding an alternative feedstock for polyurethane has become highly desirable for both economic and environmental reasons. However, due to the high cost of the petroleum-derived products or to environmental hazard, a growing effort has emerged in recent years on the research, development, and application of bio-composites. Hence, adoption of environmental friendly and inexpensive raw materials is highly necessary for the adequate protection of its citizenry and ecosystem (Iyer et al., 2014).

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Also, in the recent years, the price of crude oil has escalated raising many concerns over the stability and the sustainability of petroleum resources (Tsai et al., 2006). The rising cost of crude oil also impacts the cost of polyurethane products, because majority of the raw materials, such as polyols and isocyanates used in foams are petroleum derivatives (Abdullah et al., 2012). The preparation of polymers from renewable resources is of significant economic and scientific importance.

Moreover, nowadays, there is a great interest in finding new pure calcium carbonate sources (Nunes*et al.,* 2000). Calcium carbonate obtained from bones flour, does not contain the same bioavailability of calcium obtained from synthetic sources. Calcium carbonate from oyster shells contains lead vestige among the others potential toxically elements such as aluminum, cadmium and mercury (Mothe' et al., 2002).

However, eggshells have a number of excellent properties that can be utilized in reproducing valuable polymeric materials. The eggshells are characterized by their $CaCO_3$ compositions (Amu et al., 2005). These characteristics qualify eggshell as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories (King'ori, 2011). These eggshells are waste materials from hatcheries, homes and food industries. However, eggshells have multiple uses in fertilizer, nutrition and medicine (Amu *et al.*, 2005; King'ori, 2011). On the other hand, eggshell has advantage for not containing toxic elements (Guo et al., 2010). Egg-products industries produce great amount of shells and their final destiny is an environmental impact challenge.

This work is aimed at investigating the effect ofeggshell on the mechanical properties of flexible polyurethane foam. The lack of information on these subjects suggests that there is a promising area to be explored. In this context, the main objective of this study was to investigate the effect

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or behavior of calcium carbonate obtained from egg shell comparing to industrial calcium carbonate.

2.9.2 Uses of Eggshells

Eggshells contain calcium and trace amount of other micro elements such as magnesium, boron, copper, iron, manganese, molybdenum, sulphur, silicon and zinc (King'ori, 2011). Eggshell calcium is probably the best natural source of calcium which is about 90% absorbable and it is a much better source of calcium than limestone or coral source (King'ori, 2011).

Chicken eggshells are waste materials that can be used as an alternative soil stabilizer like lime source; they have the same composition (Amu *et al.*, 2010). Sanitized eggshells are used to increase mineral content of compost and spread around plants to deter slugs and snails. Discarded eggshells are often used as a plant fertilizer. This is because eggshells contain calcium. Making eggshell fertilizer is inexpensive and environmental-friendly, since the process reuses material to promote plant growth. Ground eggshells are effective liming sources (Guo et al. 2010).

2.11 Foam Properties Test

Some important test that are carried out to ascertain the quality of flexible polyurethane foam include among others:

2.11.1 Compressibility Test

The value obtained from this test is a measurement of the ability of foam to recover after subjected to constant deflection compression. The compression set can simply be defined as the difference between the initial thickness and final thickness of foam as a percentage of its original thickness.Mathematically, it is expressed as:

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Compression set = $(T_o-T_f)*100/ T_o$ 2.1

Where, Tois the original thickness of the test-piece and T_f is the thickness of the test-piece after recovery. Whenever the value of compression set is obtained is reported, test conditions must also be stated and these are: level of compression, time and temperature (Umar, 2010).

2.11.2 Indentation Hardness Test

The indentation hardness index of foam is measurement of its load-bearing properties. In real terms, the index is the force required to depress by 25%, 40 % and 65% a small circular plate into the foam. The testing machine is capable of indenting the test-piece between a supporting surface and an indenter which has a uniform relative motion in a vertical direction (Umar, 2010).

2.11.3 Tensile Test

A tensile test gives information about the elasticity of foam and also indicates the strength of the foam under tension. By definition therefore, tensile strength is the maximum force required to break a test- piece, divided by the original cross-sectional area. The elongation at break is the change in gauge length of the test piece, determined at the time of break, and expressed as percentage of its original gauge length. The elongation at break as a percentage is given by equation 2.2:

Elongation at break = $(L_1 – L_o)$ □ $L_o \times 100$ …….2.2

(Makanjuola, 1999)

Where, L_o is the initial gauge length and L_1 is the final gauge length where as the average tensile strength in kN/ m^2 is given by equation 2.3:

Tensile strength (young modulus) = Stress □ Strain ……...2.3

Stress = breaking load □ original cross sectional area (csa = width* thickness) ……..2.3a

Strain = extension □ original gauge length ……...2.3b

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Rajput, (2006) and Fried, (2009).

2.11.4 Density Test

The measured density of any foam is an apparent or bulk density and not polymer density. Density of foam has a parallel relationship with both its cost and load-bearing ability. High densities will generally result in higher costs and improved load-bearing properties.The apparent density is a ratio of mass to volume of foam sample expressed in kg/m^3 and is given by equation 2.4:

Apparent density (D) = Mass (M) □ Volume (V) ……...2.4

2.11.5 Hysteresis

Hysteresis is another laboratory test used to determine foam's ability to retain its original firmness properties. Hysteresis is measured by first indenting the foam sample 25 % and measuring firmness, then indenting it 65 % and again measuring firmness and finally releasing indentation to the 25 % level without allowing the foam to completely relax. Without fully releasing indentation, foam won't recover all of its original 25 % firmness, but the percentage of firmness it does recover is believed to be a good indicator of overall cushion durability. A good Hysteresis rating also contributes to how easy it is to "get out" of a sofa or other furniture piece that is designed for people to sit deeply into the seat (Umar, 2010).

2.11.6 Air Flow

Air flow is an important diagnostic test. Foam performance is optimized when air flow is maximized. This indicates that cells are open and as flexible as they should be. A good "rule of thumb" for air flow in flexible polyurethane foams is a minimum of 2.0 cubic feet per minute (cfm^{-1}) (Umar, 2010).

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CHAPTER THREE

3.0 MATERIALS, EQUIPMENT AND METHODOLOGY

This chapter presents the list of equipment/materials that were used in the course of this research and also the methodology adopted in the work.

3.1 Materials

The major materials used in work are:

(i) PolyolKonix (KE 199) polymer polyol, Korea Polyol company Ltd Korea

(ii) Toluene diisocyanate (TDI), Orinate T80, OCI Company, Ltd Korea

(iii) Amine, Tegoamin (DMEA), Evonik Industries Ltd Belgium

(iv) Distilled water machine, Aquatron (A4000), ChED., Kaduna Polytechnic, Kaduna

(v) Stannous octoate (Kosmos 29), Dow Chemicals, Europe

(vi) Silicone oil, Tegostab (8110), Evonik Industries Ltd Belgium

(vii) Mineral calcium carbonate, West African Solid Mineral Company, Industrial grade

3.2 Apparatus

(i) Beakers (Pyrex), 1000 ml and 500 ml

(ii) Measuring cylinders (Pyrex), 1000 ml and 500 ml

(iii) Laboratory mortar and pestle

(iv) Sieves; Gilson Automatic sieve Tester, SS – 15 (45, 63 and 90 μm)

(v) Spatula (Stainless steel)

(vi) Buckets (Plastic) Eleganza, 10 ltrs

(vii) Syringes (5 ml), Zarinject

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(viii) Clinical Thermometer, Seal (-10 to 360 ^{o}C) England

(ix) Cardboard mould (box)

(x) Stop watch (hand held set) SGH-1537, Samsug, Korea

Table 3.1: List of other equipment used in this work and their specifications

S/No.	Equipment	Model/Type	Source
1.	Digital weighing balance	OHAUS USA/Scout pro;SPU2001(150kg/330lb)	ChE.D ABU Zaria.
2.	Indentometer	Hampden; mechanical Tester (EC30).	Royal Foam, Kano
3.	Electric Water Bath Compression device	IWB 002, 250×250 Intertek Plastics Technology, ASTM D 395	ChED ABU Zaria Jafco (Unifoam) Nig. Ltd., Kaduna.
4.	Knife edge cutting machine	Sunkist Chemical Machinery Ltd., Taiwan. S-2AC (397.5in×32mm×0.5mm).	Jafco (Unifoam) Nig. Ltd., Kaduna.
5.	Mixer	(Fisatom, 710, sharf-stiring device, P: 25W, R: 25-200 rpm).	ChE.D ABU Zaria
6.	Oven	Hot-Air, Drying, Temp. range:50-220 ^{o}C) DHG-9101 S.N	Food Tech.Dept., Kaduna Polytechnic
7.	XRF machine	Oxford Inst., X-Supreme 8000)	Chem.Dept. ABU Zaria.
8.	SEM Machine	PHENOM Pro-X at 15kV	ChE.D ABU Zaria.
9.	Electric Ball mill	OVERVELD-KERA b.v SOESTERGERG, Holland (Kw: 0.37; Type : V14)	Mining Engr'g., Dept.Kad. Poly., Kaduna.

3.3 Materials, Preparation and Methodology

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The raw materials used for the production of flexible polyurethane foam were obtained from JAFCO Nigeria Ltd., Kudenden, Kaduna State, while the eggshells were collected from eateries within Kaduna Metropolis.

3.2.1 Preparation of Eggshell

The eggshells (filler material) were collected from the waste bins of food industries at various locations within the Kaduna Metropolis. The eggshells were washed thoroughly and dried to constant weights at 80^{o}C for 24 hrs in an electric oven. They were then crushed with hammer and grounded into fine powder using an electric ball milling machine for 6 hours and stored in polythene bags.

3.2.2 Beneficiation of Eggshell

Eggshell of 2.30 kg weight was soaked in about 8 litres of water mixed and then thoroughly before being allowed to settle for 24 hours. It was remixed and the liquid was decanted from the mixture to remove all sorts of impurities (dirt) contained in it. About 6 liters of water was added to the remaining mixture and allowed to settle. The same procedure was repeated for another five days. The remaining eggshell solution was poured into an open container, where it was allowed to dry for four days. The air dried eggshell was weighed and transferred into an oven to further dry at 80^{0}C until there was no change in weight of the beneficiated eggshell. The caked eggshells in lumps were broken to powder in a mortar with piston.

3.2.3 Sieve Analysis

The particle size distributions of eggshells were determined by the Gilson Automatic sieve Tester; (SS-15) model attached to the following mesh sizes 90µm, 63µm and 45µm.

Table 3.2: Elemental composition of raw eggshell

S/N	Compound	Concentration, wt%

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1.	MgO	0.872
2.	Al_2O_3	0.884
3.	SiO_2	3.478
4.	P_2O_5	0.472
5.	SO_3	0.812
6.	Cl	0.223
7.	K_2O	0.150
8.	CaO	92.317
9.	TiO_2	0.053
10.	Cr_2O_3	0.018
11.	Fe_2O_3	0.379
12.	SrO	0.341

Table 3.3: Elemental compositions of the beneficiated eggshell

S/N	Compound	Concentration, wt%
1.	MgO	0.594
2.	Al_2O_3	0.618
3.	SiO_2	2.896
4.	P_2O_5	0.330
5.	SO_3	0.719
6.	Cl	0.133
7.	K_2O	0.135
8.	CaO	93.672
9.	TiO_2	0.051
10.	Cr_2O_3	0.018
11.	Fe_2O_3	0.483
12.	SrO	0.351

Table 3.4: Chemical composition of mineral calcium carbonate

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S/N	Compound	Concentration, wt%
1.	Al_2O_3	0.5
2.	SO_3	0.11
3.	CaO	97.27
4.	TiO_2	0.03
5.	Fe_2O_3	0.094
6.	Y_2O_3	0.45
7.	Ag_2O	1.35
8.	CeO_2	0.05
9.	Sm_2O_3	0.03
10.	Yb_2O_3	0.08
11.	Lu_2O_3	0.08

3.3 X-ray fluorescence (XRF)

X-ray Fluorescence (XRF) analysis is to be done to determine the elemental composition and analysis of the samples. The sample is to be loaded into the plastic sample container which has a thin plastic surface that allows the passage of X-ray beaminto the sample. The sample holder positioned into the pan of the X-ray equipment (model P.W 4030/45B). This equipment has twelve compartments for samples to be analyzed simultaneously and its progress being measured using a computer monitor.

3.3.1 X-ray Diffraction Techniques

X-ray Diffraction (XRD) analysis is to be carried out to determine the mineralogical structures or phases. The mineralogical phases for $CaCO_3$ will be determined using a SCHMADZU Model 6000 XRD diffractometer. The $CaCO_3$ samples are to be pulverized to meet the required

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equipment specification. The samples will be dried for one hour at 60^{o}c and allowed to cool to room temperature, then mounted on mounted on a specimen holder of the diffractometer. The samples are to be set and screened between the angles of 2.0 and 65 degrees at a speed of 3.0 degrees per minutes which runs for 21 minutes. The diffractograms will be displayed automatically and processed using the accompanied Schmadzu diffractometry software.

3.4 Determination of Chemicals Consumption Rate

The amount of chemicals used in the production was calculated based on existing procedure (Makanjuola, 1999). All foaming formulations are based on the amount of polyol being equal to '100 parts by weight' or '100 p.b.w'.

3.4.1 Determination of water content

The approximate water level required for the production of flexible polyurethane foam was adopted from Makanjuola, 1999. For the targeted density of 20kg /m^3, a water level of 5.0 parts per hundred of polyol was used.

3.4.2 Determination of toluene di-Isocyanate (TDI) content

TDI is consumed at two different stages during the foaming process:

I) Reacting to Water.

Amount of TDI required reacting with water

= (parts of water) × 9.67 (conversion factor)…….,…….4.1

II) Curing of Polyether.

Amount of TDI required for curing of the foam

(Hydroxyl number = 50 (from polyol manufacturing company).

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= (hydroxyl number) × 0.152 (conversion factor) ……...4.2

3.4.2.1 Hardening of the Foam

A blow index range of 100-110 is required (Makanjuola, 1999). In this work a blow index of 102 was assumed.

Therefore, total amount of TDI = (102/100) × (I+II)…….....4.3

3.4.3 Determination of Silicone Content

The amount of silicone in a formulation varies with the density of foam. It is also dependent on silicone type: weak, medium or strong. The medium was used for this research work; a silicone content of 1.02 was adopted from Makanjuola, (1999).

3.4.4 Determination of Amine Content

The amount of amine required is dependent on the type and source. The amount is also dependent on the intensity of the reaction; a normal reaction is achieved when the foam mixture starts to cream after 12-14 seconds. Dimethyl-ethyl-amine (DMEA) which the most popular type in Nigeria was selectedand 0.28 p.b.w content used for this work was also adopted from Makanjuola, (1999).

3.4.5 Determination of Stannous octoate Content

The foaming process can be extremely sensitive to the amount of stannous octoate used. Tolerance limits are very narrow as a deviation of just 10% may cause a major deformity. The amount of stannous octoate for 20 kg/m^3 was also adopted from Makanjuola, (1999). The tin catalyst has a range of 0.27-0.33p.b.w for densities below 25kg/m^3. This is shown in Table 3.5

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3.4.6 Determination of Filler Content

Ideally, the presence of fillers should not significantly affect any normal chemical reaction, but some minor adjustments in the level of activators (especially stannous octoate) are necessary. In this work eggshell and mineral calcium carbonate at loading of 5wt%, 7.5wt%, 10wt% ,12.5wt% and 15wt% of particle sizes 45µm, 63µm, and 90µm for the eggshell and as for the mineral calcium carbonate (calcite), 63 µm particle size was considered in keeping with the Nigerian industrial standard.

Table 3.5: Summary of Foam Formulation

Chemicals	P.B.W
Polyol	100.00
TDI	57.00
Water	5.0
Amine	0.12
Silicone	1.02
Stannous Octoate	0.2

For this production, 0.1kg of polyol was consumed per run, and then weight requirement of other chemicals was obtained by multiplying their respective p.b.w by a factor of 1. This is shown in Table 3.6

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Table 3.6: Summary of the actual weights of chemical

Chemicals	P.B.W	Actual Weights (g)
Polyol	100.00	100.00
TDI	57.00	57.00
Water	5.0	5.0
Amine	0.12	0.12
Silicone	1.02	1.02
Stannous Octoate	0.28	0.28

3.5 Foam Production

The laboratory mix (box foaming) was used for the foam production in this work.

3.5.1 Preparation of Flexible Polyurethane Foam

The polyol, toluene diisocyanate and fillers with particle size of were accurately weighed into separate beakers using triple beam balance. The other raw materials required in small quantities were measured with syringes. The measurement of raw materials were based on part per hundred of polyol. Polyol and the filler were placed in a plastic receptacle, and the mixture was stirred until complete homogenization. Next, the amine, surfactant and water were added. The mixture was submitted to mechanical stirring for one minute. Shortly after the Tin (stannous octoate) catalyst was added and the mixture was stirred again for 30 seconds. After introducing the isocyanate, the mixture was submitted to 10 seconds of stirring and thenthe whole mixture was thensmartly poured into a prepared cardboard mould of the dimensions 15cm*15cm*20cm. A stopwatch was used to monitor the rise time of each foam sample, and foam sample was allowed

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to cure for 24 hours in the mould.Then, the cured foam blocks were cut to standard sample sizes for analysis. Thereafter, the foam samples produced were subjected to mechanical properties test such as compression, hardness, elongation, tension, heat ageing and density tests using the compression set, hardness index (indentation force deflection), elongation at break, tensile strength, heat ageing elongation at break and tensile strength and density tests.

3.6 Characterization of Polyurethane Foam

Test samples were cut from the foams produced into standard sizes suitable for the respective tests and the foam's surface skins were avoided. Three test samples each were used for all the tests and the mean values recorded were used as representative values of the properties.

3.6.1 Compressibility (compression set) Test

The compressibility (compression set) test was carried out using a compression device as shown in Plate I.1 (Appendix I). The test specimen were cut according to ASTM-D 3574 standard dimension of 0.5cm*0.5cm*0.25cm. All test-pieces were kept free of any contamination and skin on the vertical sides. It is noteworthy, that as long as the original sample thickness is less than the sample length and width, compression set is independent of sample thickness. Each test sample was placed the compression device which consists of two flat plates having dimensions larger than those of the test-pieces.

The provided spacers and clamps were arranged such that the plates were held parallel to each other and space between the plates was adjusted to the required deflected height. The test-pieces were compressed to 75% of their original thickness and maintained under constant condition for 22 hours. Then, each test-piece was removed from the apparatus and was placed on a wood.

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Then, the test-pieces were allowed to recover for 30 minutes and thereafter, their respective thicknesses were re-measured.

Plate I.1 shows the arrangement of foam sample into compression test device (Appendix I). Finally, the compression set for each test-piece was calculated mathematically based on the initial and final dimensions using standard shown in Equation 2.1.

3.5.2 Indentation (Hardness) Test

The indentation hardness test was carried out in an indentation machine (Hampden mechanical Tester; EC30) as shown in Plate I.2 (Appendix I). The test specimens of dimension 0.15cm*0.15cm*0.20cm were positioned on a support plate, so that the center of the specimens were located below the center of the indentor (diameter = 0.35cm). The support plate was perforated to allow for free flow of air. A force of 5N was applied to the test area and the thicknesses of the test-piece measured. The specimens were indented at rate of 100mm/min. to produce an indentation of 75% indentation (25% thickness of the original test sample), the applied force was released. This loading and unloading was repeated two times more and immediately after the third unloading the specimens were indented to 40% of their thicknesses. Each time, the deflection was maintained for a period of 30 seconds and the corresponding forces in Newtons were displayed on the monitor which were noted and recorded as the indentation hardness index. The same procedure was repeated for 40 and 65% thickness of residual test sample. The arrangement of foam sample in the hardness test machine can be found in Appendix I.2.

3.5.3 Tension (Tensile Strength) Test

Three samples each for the test were die-cut into “dumb-bell” shape. The thickness, width and gauge length of each test piece was measured at five evenly distributed points on the test-piece

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and the average found. The test-pieces were placed in the grips of the testing machine and care was taken to ensure that the test-pieces were symmetrically positioned so that tension is distributed uniformly over the cross section. The machine was then turned on after which maximum force and the distance between the inside edges of the two reference lines were measured immediately prior to the break of the test-pieces. The maximum forces and elongation results were monitored from the monitor screen and recorded. Finally, the elongation at break and tensile strengths were calculated using the standard equations 2.2, 2.3, 2.3a and 2.3b. The same procedure was repeated for samples after heat aging test. The "dog bone or dump bell" shaped test piece for elongation and tensile strength tests is shown in Plate I.3 and the arrangement of test sample clamped in tensile strength test machine is shown in Plate I.5 (Appendix I).

3.5.4 Density Test of the Foam Sample

Three test-pieces each were each tested using weighing balance capable of weighing to an accuracy of 0.01g, the values were initially in grams and were also converted then to kilo grams and their respective values recorded. The dimensions of the test-pieces were measured using meter rule in centimeter and were converted to meters. Each sample weighs were the divided by their respective volume calculated using Equation 2.4 and the mean values recorded to get the desired density. Arrangement of test samples on weighing scale for density test is shown in plate I.4 (Appendix I).

3.5.5 Scanning Electron Microscopy (SEM)

The structure of foam composite was examined by using Scanning Electron Microscopy (SEM) of PHENOM Pro-X and the foam was coated with thin layer gold by Auto Fined Coaterof Quorum 15OR E.S. The foam specimen of 0.5 mm*0.5 mm*0.5mm was prepared in order to fit

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with the specimen holder used in SEM. The small foam was mounted on the holder using a double side carbon tape. During the SEM examination, the mean cell size of foam structure was measured directly according the micrograph captured using analytical SEM software.

CHAPTER FOUR

4.0RESULTS AND DISCUSSION

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The results of the beneficiation, XRF analysis for eggshell and calcite, characterization and analysis of foam samples produced are presented in this chapter. Three test-pieces cut were characterized for each mechanical property and their mean values recorded. Statistical package for Social Science (SPSS) 16.0 for window software was used to perform a descriptive (std. error, std. deviation and variance) statistics at 95 % level of confidence. Detailed statistical analyses are presented in Appendix A to H.

4.1 Beneficiation of Eggshell Particles

After five successive beneficiation batches were carried out, 2.27 kg of dried beneficiated eggshell particles were obtained from the 2.30 kg of raw eggshell, owing to the rigorous sieving and decantation procedures. The result of XRF in the table 3.1 shows that, the eggshell contains 92.317 wt% calcium carbonate but after beneficiation, the CaO content increased to 93.672 wt% as shown in Table 3.2. Asimilar value was reported by Amu et al., (2005) for dry eggshell. It can also be observed from the table that, the CaO content increases with beneficiation, which suggest that, the goal of beneficiation process aimed at increasing ratio of calcium carbonate to silica was achieved. The oxide impurities in the beneficiated eggshell also reduce from the raw eggshell but less significantly except for silica, as expected. The remaining mineralogical composition such as MgO, Al_2O_3, P_2O_3, SO_3, Cl, K_2O, TiO, Cr_2O_3, Fe_2O_3, and SrO were in traces, while SiO_2 reduces from 3.478 wt% to 2.896 wt%. However, the result of XRF analysis also showed 97.27 wt% CaO in calcite and ispresented in Table 4.3. Tables 4.1, 4.2, and 4.3 show the elemental composition of raw, beneficiated eggshell and mineral calcium carbonate respectively.

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4.2 Effect of Fillers Volume Fraction and Particle size on Compression Set of Flexible Polyurethane Foam

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Figure 4.1 presents the effect of filler Volume fraction and particle sizes on the compression set of flexible polyurethane foam. Detailed calculation and statistical analysis are shown in Appendix A.

The compression set measures the difference in dimension before and after compression. From Figure 4.1, it can be seen that, the compression set of the filled foam samples were found to increase with increased filler content and particle size from 5 wt% to 15 wt% and 45µm to 90µm respectively.

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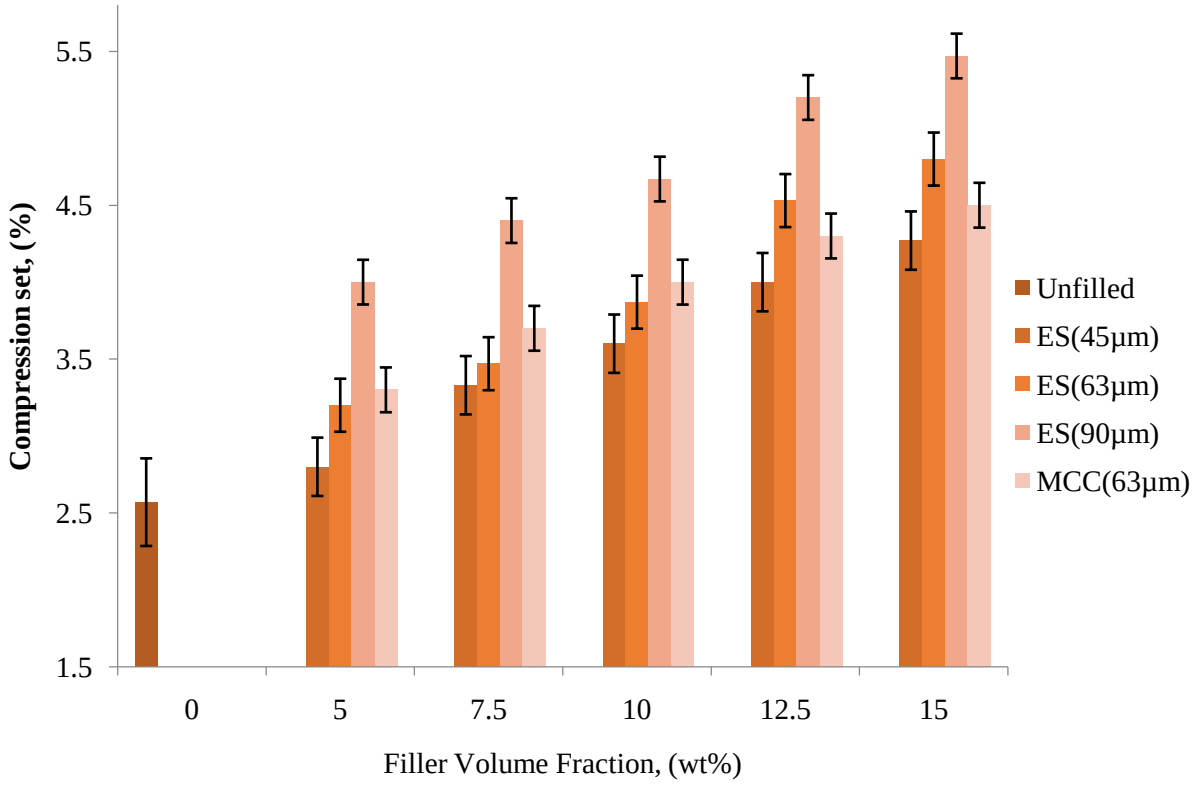


Figure 4.1:Effect of Fillers Volume fractions and Particle Sizes on Compression set of FlexiblePolyurethane Foam

The unfilled (control) which is the control sample foam recorded the lowest value of 2.57% for compression set test, which implies that fillers reduce the tendency of the foam to return to its original size after compression. A similar observation was reported by Onuegbu*et al.*, 2010 in the studies on the effect of animal waste (Goat femur) on the mechanical properties of flexible polyurethane foam. The compression set of 63µm goat femur at 10% filler load was found to have a value of 3.64% close to that of 10wt% mineral calcium carbonate filled foam used as control. From Figure 4.1, it can seen that among the filled foam samples, 45µm-sized eggshell filled foam at 5wt% filler load had the lowest compression set with a mean value of 2.80% closest to the control with standard error and deviation of 0.4619 and 0.8000, respectively.

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Followed by 63µm-sized eggshell and mineral calcium carbonate filled foams, then the 90µm-sized eggshell filled foams at the same filler load respectively and the lower the value of compression set the better. The eggshell filled foams compared favourably to the mineral calcium carbonate for the same particle size at most filler loading with the former slightly lower than the later as indicated by error analysis and depicted by the error bars. This implies that, both fillers showed no significant difference on this property. However, it was revealed from Figure 4.1 that all foam samples produced fell within the ASTM D-3574 set standard range of 1-10% (NIS 295:1993) for compression tests of polyurethane foams, with the unfilled foam sample having a value (2.40%) closet to the minimum standard. It can also be observed that, the filled foams had higher compression set compared to the control (unfilled) foam. Therefore, the fillers could probably stiffen the foams matrices making them not to regain some of their dimensions after compression. The result also indicated that among the filled foam samples, the compression set of eggshell filled foams were lower than those of mineral calcium carbonate as shown in Figure 4.1. This shows that eggshell filled foams are better in terms of this property.

4.3 Effect of Filler Volume Fractions and Particle Sizes on Hardness Index of Flexible Polyurethane Foam

Figure 4.2 presents the result of effect of filler compositions and particle sizes on the hardness index of the produced flexible polyurethane foam. The detailed calculation and statistical analysis are shown in Appendix B.

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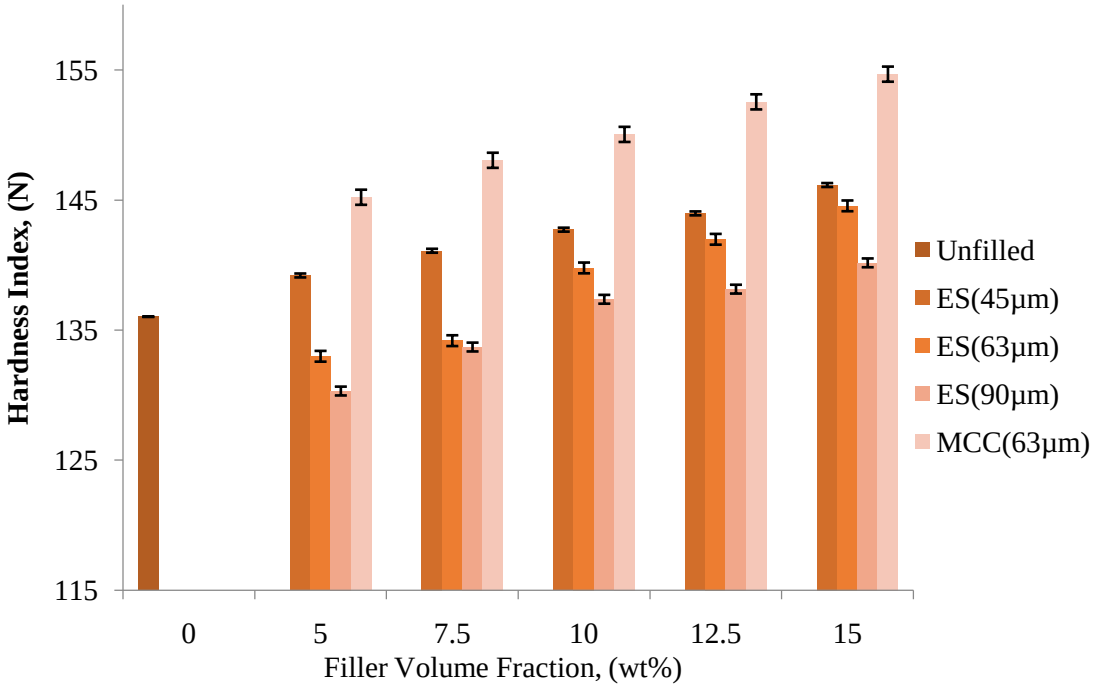


Figure 4.2: Effect of Filler Volume fractions and Particle sizes on Hardness of Flexible Polyurethane Foam.

The figure showed an increase in hardness with increased filler content for both fillers and decreased particle size in the case of eggshell filler compared to the unfilled foam. From the figure it can be observed that the hardness index of 63µm and 90µm eggshell filled foams initially dropped at 5wt% and 7.5wt% filler contents compared to the control (control) foam sample and both particle sizes seem to have the same effect on the hardness index at the 7.5wt% filler load. This can be explained by the overlap of their respective error bars on the chart in Figure 4.2. The hardness index of filled foam is expected to be higher than that of the unfilled foam. However, the decreased hardness property by the filler particles was probably due to either agglomerated particles not well dispersed in the polymer, thereby creating stress concentrations

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in the polymer matrix and decrease hardness or the filler particles did not allow a complete formation of plateau border area and cell windows by draining excessive liquid polymers from the cell struts thereby weakening the hardness strength of the foam. The finer filler particles showed improved property than the coarser filler particles. This indicates that, fillers become increasingly reinforcing as their particle size decreases. From the result, it is obvious that filled foam samples have higher load bearing ability than the unfilled foam sample.

Moreover, the increase in the hardness of foams by micro fillers was due to the random dispersion of the fillers into the polyurethane matrix (Ganiyu *et al.*, 2010). In Figure 4.2, the unfilled (control) content foam sample had hardness index of 136.03N having a standard deviation and standard error values of 0.03000 and 0.01732 respectively as can be seen from the statistical table in Appendix G. The result of indentation hardness shows that, the mineral calcium carbonate filled foam samples have higher hardness than those of eggshell filled at all level of filler compositions and the same particle size with the highest value (154.67 N) being that of 63µm mineral calcium carbonate at 15wt%. That is, its maximum load carrying capacity was the highest among all the foam samples, and the filled foams were higher than the unfilled foam for hardness index. However, the hardness property of all the foam samples filled with eggshells fell out of the NIS 295 and ASTM D-3574 range of 147 – 170N expected for good foam with that filled with 45µm sized eggshell particle at 15 wt% being the closest to the minimum Nigerian industrial standard (NIS 295: 1993)and American standard test methods (ASTM D-3574) having a mean value of 146.70N with standard deviation and standard error of 0.05774 and 0.41802 respectively as shown in Table G.8 (Appendix G) and the mineral calcium carbonate filled foam samples at all filler loading except at 5wt% fell within the set standards. Since the result showed that, for the eggshell filled foams, a corresponding increase in hardness

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index with increased filler content and decreased particle size then, it implies that the higher load bearing capacity could be achieved at lower particle size and higher filler content in the foam production. The result also, indicated that, mineral calcium carbonate filled foams were better than eggshell filled foams in term of hardness index.

4.4Effect of Filler Volume Fractions and Particle Sizes on Elongation at Break andTensile Strength of Flexible Polyurethane Foam

The Figure 4.3 shows the elongation at break of the foam samples filled with different content of mineral calcium carbonate and eggshell while Figure 4.4 shows the tensile strength of the foam samples both fillers. The detailed calculation and statistical analysis are shown in Appendix D and E.

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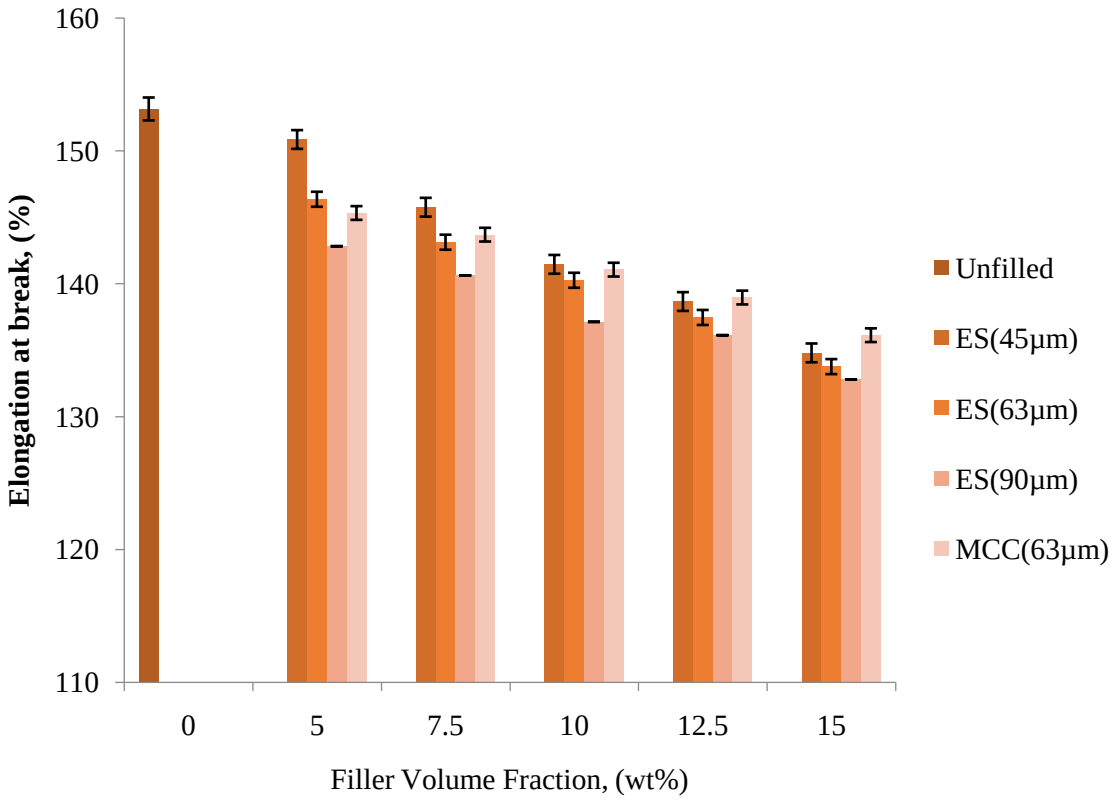


Figure 4.3 Effect of Filler Volume fraction and Particle sizes on Elongation at break of Flexible Polyurethane Foam.

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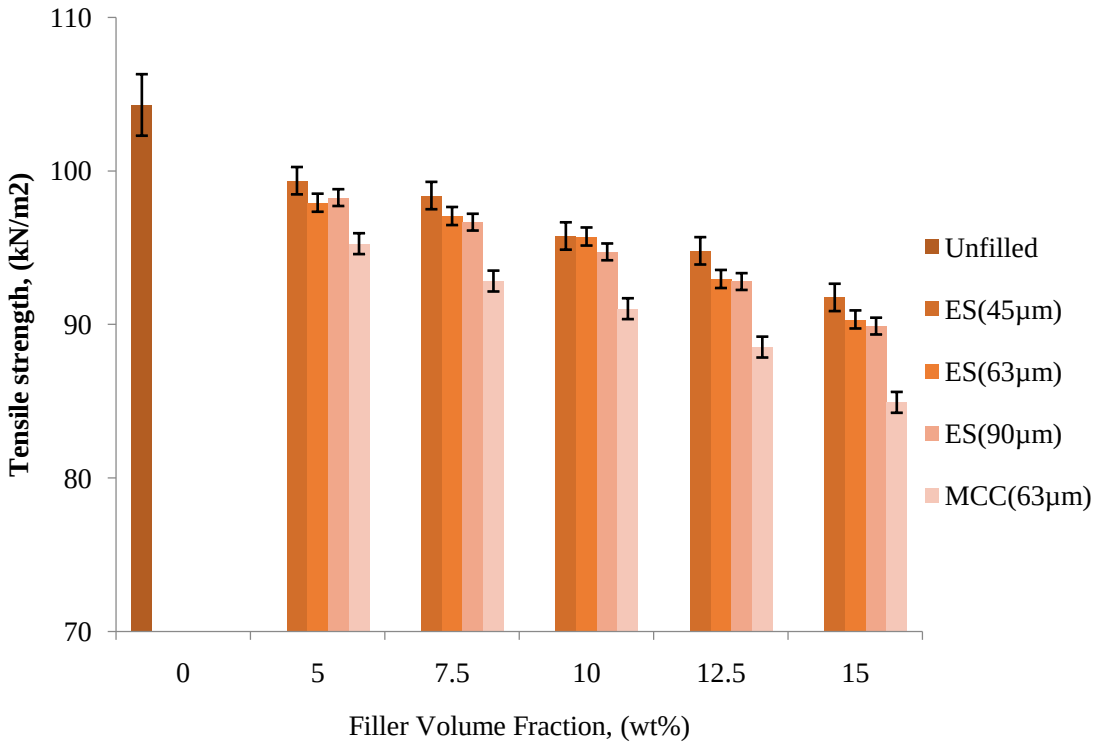


Figure 4.4: Effect of filler Volume fraction and Particle sizes on Tensile strength of Flexible Polyurethane Foam.

The elongation at break (defined as the extent to which a foam sample can be stretched before it breaks expressed as a percentage of its original length) and the tensile strength (defined as the resistance of a material to a force tending to tear it apart, measured in kilo Newton per square meter) of flexible polyurethane foams reinforced with both fillers are plotted against filler contents 5 – 15wt% in Figure 4.3 and 4.4 respectively. For all particle sizes, the tensile strength and elongation at break decreased while on the other hand increasing the load of the filler weight percentages compared to the control. However, the tendency with which the coarser filler reduce the property was not as much as for the fine fillers. The decreased mechanical properties of filled foams are probably due to the fact that there was agglomeration of the coarse fillers, as a result of excess particles that were not well dispersed in the polymer which created stress

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concentrations in the polymer matrix and thereby decrease the tensile strength and elongation at break of the foams. Higher elongation indicates higher ductility and higher tensile strength indicates the maximum tension the material can withstand without tearing (http://www.thefreedictionary.com/tensile+strength). However, the use of fillers was observed to affect these properties with 45µm eggshell filled foam sample at 5 wt% composition being highest with values of (151.20%) elongation at break and (99.37kN/m^2) tensile strength having standard deviation and standard error of (0.6110 and 0.3528)and (0.8737 and 0.5044) for elongation at break and tensile strength respectively. This response is a characteristic of materials reinforced with stiff inorganic materials as was observed by (Ganiyu *et al.,* 2010 and Isa *et al.,* 2012). It was also observed from the results that, the control sample (100% polyol) foam had an elongation of 153.20% and tensile strength of 104.3kN/m^2 both of which fell within ASTM D 3574 minimum standard as can be seen in Figure 4.3 and 4.4. The descriptive statistics at 95% level of confidence showed that, the control sample had standard deviation and error of 0.3786 and 0.2186 respectively, for elongation while for tensile strength the control had standard deviation and error values of 3.4699 and 2.0033, respectively. The result indicated that, the tensile strength of the eggshell filled foams samples for the 63µm sized particle compare favourably with those of mineral calcium carbonatefilled foam samples for all filler volume fractions. The result shows that there is no significant difference between the eggshell and the mineral calcium carbonate as depicted by the error analysis. From Figure 4.3 at 10wt%, 12.5wt% and 15wt% filler loadings, the same trend was observed for elongation at break as explained by the error bars on the chart. The results also, indicated that 45µm eggshell foam samples at 5wt% filler content had tensile strength and elongation at break values closest to the control and conformed to ASTM D-3574 standard. The elongation point at break and tensile strength of good

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foam, according to ASTM D-3574 should have minimum value of 150% (whereas according to the NIS 295 1993 it should have minimum value of 120%) and 98kN/m^2 respectively. However, the result of elongation at break and tensile strength showed that, all the filled foams had values outside the Nigerian industrial standard except 45µm-sized eggshell filled foams at 5 and 7.5wt% for tensile strength and 5wt% for elongation at break. The results indicated that, tensile strength and elongation at break responses of the fillers used for this research (mineral calcium carbonate and eggshell) compare favorably at the same level of particle size and filler loading. The results also, indicate both tensile strength and elongation at break of 63µm-sized mineral calcium carbonate filled foam samples were lower than those of the eggshell filled foam samples at the same level of particle andfiller loading. This implies that eggshell filled foams are better in terms of these properties.

4.5 Effect of Filler Volume Fractions and Particle Sizes on Heat Ageing Elongation at break and Tensile strength of Flexible Polyurethane Foam

Figures 4.5 and 4.6 present the effect of filler compositions and particle sizes on the tensile strength and elongation at break of flexible polyurethane foam after heat ageing test. The detailed calculation and statistical analysis are shown in Appendix F and G.

The heat ageing test is usually carried out to fasten the rate of curing of the foam samples. Heat ageing test normally come up to ascertain the stability of the foam sample under very harsh heating condition for hours. It is generally taken that; this will indicate the foam stability with time. The result obtained indicated that, the 100% polyol content foam samples indicate mean values of 153.17 % and 118.77 kN/m^2, for elongation at break and tensile strength when heat aged with the standard deviation and error 0.56801 and 0.32794, respectively.

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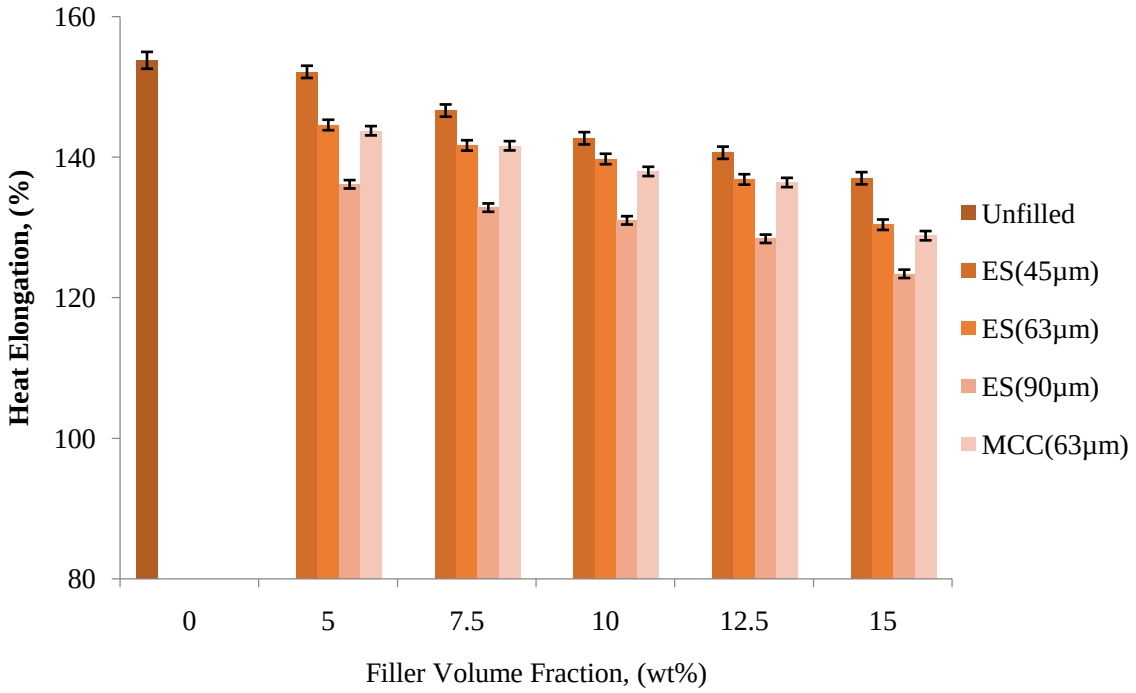


Figure 4.5 Effect of filler Volume fractions and Particle sizes on Heat Ageing Elongation of Flexible Polyurethane Foam.

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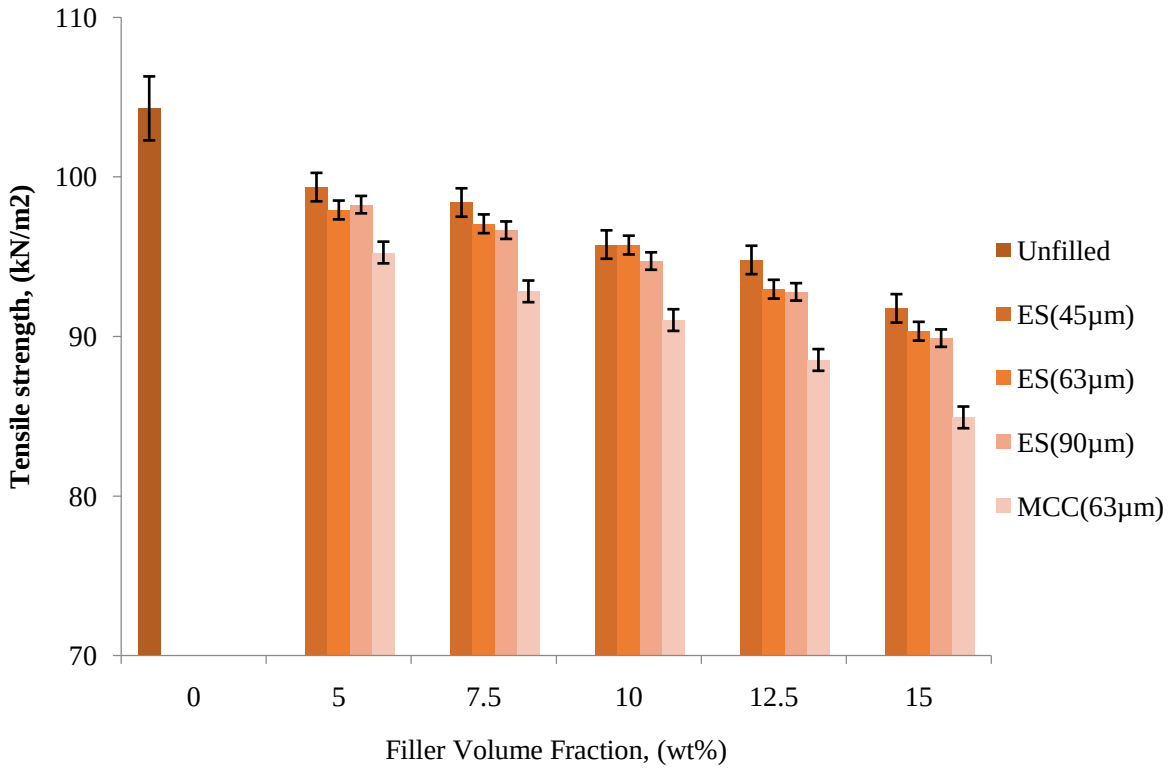


Figure 4.6: Effect of Filler Volume fractions and Particle sizes on Heat Ageing Tensile Strength of Flexible Polyurethane Foam

The elongation at break and tensile strength after heat ageing ware found to drop generally with increase in filler content from 5 – 15wt% for both fillers compared to the control samples.

The elongation at break after heat ageing of foam samples filled with 63 µm-sized particles for both fillers (mineral calcium carbonate and eggshell) compared favourably at all level of filler loading, however the eggshell filled foam samples were slightly higher than those of mineral calcium carbonate whereas the tensile strength after heat ageing for both fillers filled with 63µm particle size compared. However, those filled with mineral calcium carbonate were generally lower to those filled with eggshell at the same level of particle size and filler loading. This is better explained by the error analysis indicating that, both fillers did not show any significant

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difference in their effect on these properties. Higher elongation indicates higher ductility (www.pfa.org). However, the use of fillers was observed to affect these properties with the filled foams having values lower to that of the unfilled foam. The 45µm eggshell filled foam at 5wt% had elongation value of 152.14% closest to the minimum standard of 150% with standard deviation and error of 0.88425 and 0.51052 respectively, while tensile strength after heat ageing of 101.78kN/m^2 with standard deviation and error of 4.19266 and 2.42064 was recorded. The difference in elongation at break before and after heat ageing test of the 45µm eggshell filled foam at 5wt% composition was 0.94% with elongation at break of foam samples after being higher than those before heat ageing while the tensile strength of 45µm eggshell filled foam after heat ageing was 2.41kN/m^2 higher than that before the heat ageing. Heat ageing could have resulted in complete curing of the foam sample resulting to enhanced tensile strength indicating that probably the foam when left to cure for a period of time would have improved the tensile strength property. The result indicated that, the filled foams were lower than the unfilled for the two fillers used. Also, the tensile strengths after heat ageing were generally higher than before heat ageing; with the 5wt% foams having the highest values. The results show that the elongations at break of the eggshell filled foam samples were higher than those of mineral calcium carbonate filled foams. This implies that eggshell filled foams are better in terms of this property.

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4.6 Effect of Filler Volume Fractions and Particle Sizes on Support Factor of Flexible Polyurethane Foam

Figure 4.7 presents the effect of filler compositions and particle sizes on the support factor of flexible polyurethane foam. The detailed calculation and statistical analysis are shown in Appendix H.

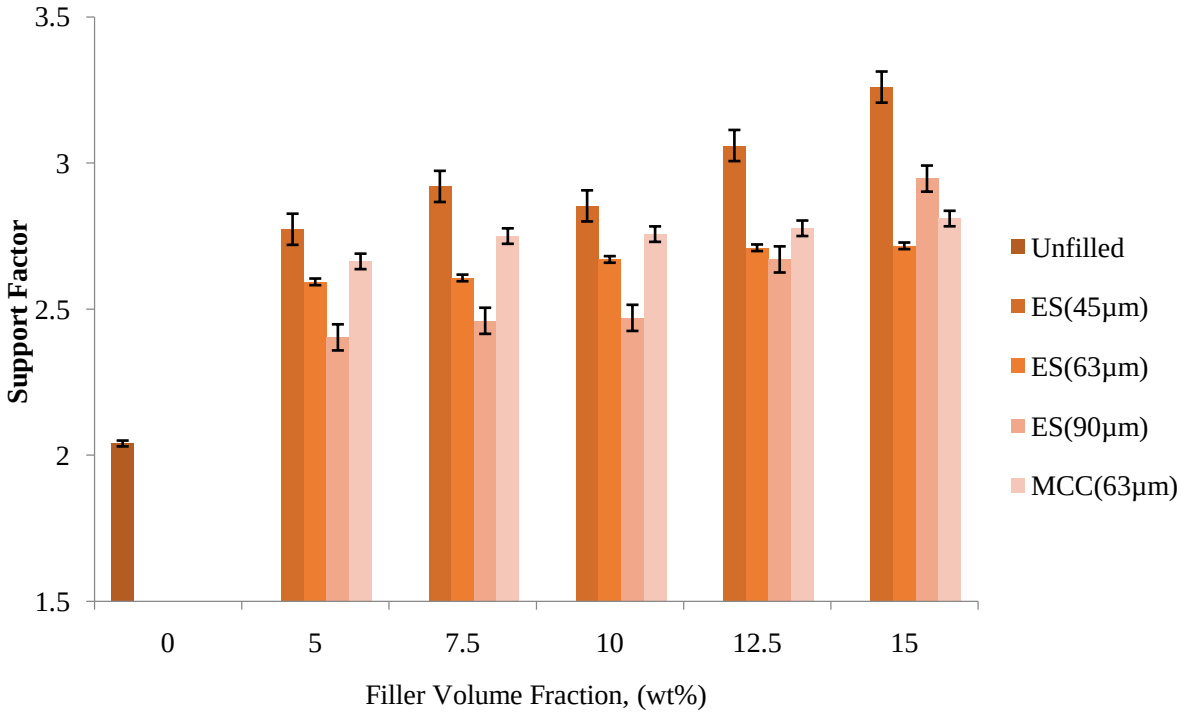


Figure 4.7Effect of Filler Volume fractions and Particle sizes on Support factor of FlexiblePolyurethane Foam.

The support factor is the ratio of 65% IFD (indentation force deflection) divided by the 35% IFD (indentation force deflection). The support factor in a grade of foam is one of the most important measures because it indicates how much weight or load factor the foam will support. Support factor is a measure of the cushioning ability of foam.

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From Figure 4.7, it was observed that, the support factor increased with increased filler loading from 5 – 15wt% for both fillers and decreased with increasing particle size in the case of eggshell filled foams. The result indicated that, the 100% polyol foam sample had a mean value of 2.05 having a standard deviation and error values of 0.01732 and 0.01000, respectively as shown in Tables H.1-H.8 (Appendix H). The higher the number of support factor, the greater the difference between the surface firmness and deep support. Higher support factors allow desirable softness a firm inner support. At 12.5wt% composition, the 45 and 90µm eggshell filled foams seem to have the same value of support factor as shown in Figure 4.7 and depicted by the error bars on the chart (Figure 4.7). However, the 45µm eggshell filled at 15 wt% foam had the highest value of 3.26 (with standard deviation and error of 0.9165 and 0.05292) for support factor among the eggshell filled foam samples but unfilled foam samplehad lowestsupport factor comparedto the filled foam samples.

Furthermore, all foam samples fell within the standard range; this implies that filled foams have the ability to provide support. The 63µm-sized calcium carbonate filled foam samples have higher values than the eggshell filled foam sample at all level of composition, though both foam samples fell within the NIS 295: 1993 and ASTM D-3574 standard limit. The support factor according to the NIS and ASTM D-3574 is expected to have a range of 2.0 – 3.5. Since the support factor of eggshell filled foam samples were lower than those of mineral calcium carbonatefilled foam samples, it then indicates that calcium carbonatefilled foams are better in terms of support factor property.

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4.7 Effect of Filler Volume Fractions and Particle Sizes on Density of Flexible Polyurethane Foam

Figure 4.8 presents the effect of filler compositions and particle sizes on density of flexible polyurethane foam. The detailed calculation and statistical analysis are shown in Appendix I.

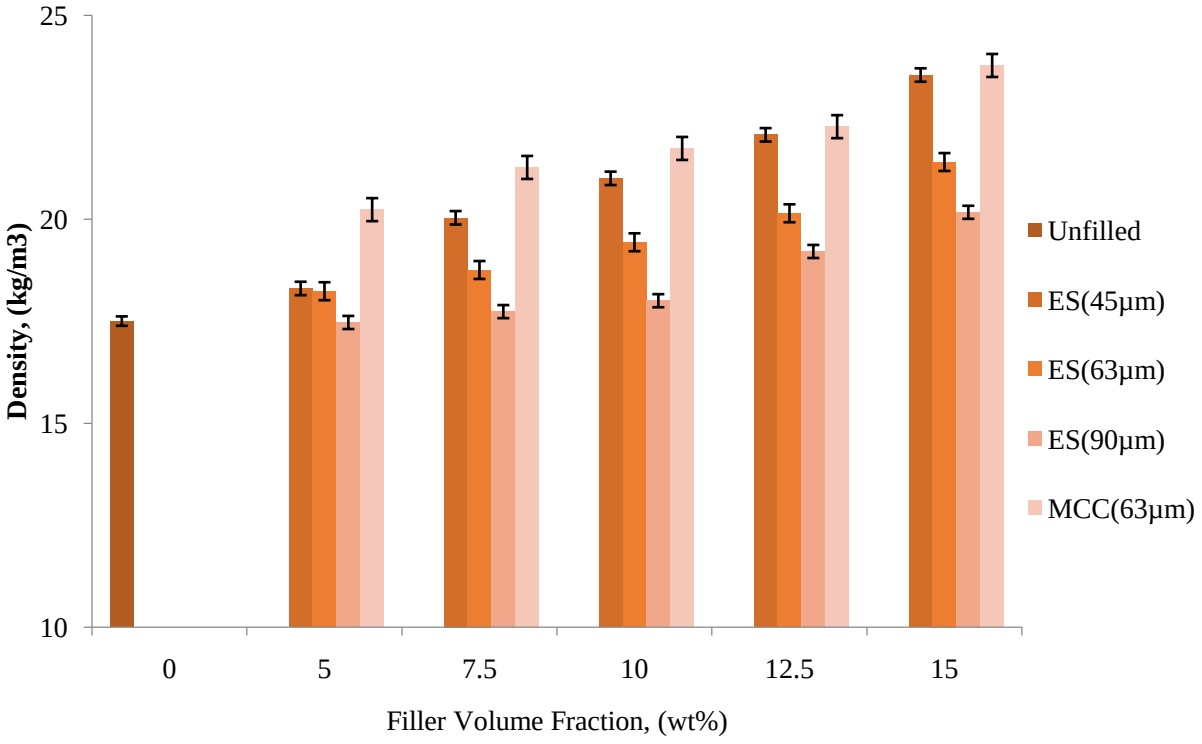


Figure 4.8: Effect of Filler Volume fractions and Particle sizes on Density of Flexible Polyurethane Foam.

Foam density is a specific measurement of how much weight in kilograms polyurethane foam can handle per cubic meter. Simply put, the higher the density the longer the foam will last (the density rating tells the strength of the foam).

As shown in Figure 4.8, the density was found to increase with increase in calcium carbonate content while it increased with an increase in eggshell content and decrease with an increased

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particle size. The smaller the particle size the larger the surface area and the more the filler polymer interaction. This could be due to the finer fillers having a large surface area to volume ratio making the fillers create a large number of small cells and closing more voids on the numerous polymer cell windows.Again, the higher the filler load, the higher the density of the foam and the extent of the improvement on the density of the foam by the two fillers are however observed to be gradual within the limits of loading studied.

The result indicated that, the control (100% polyols) content foam sample had the lowest density of 17.5kg/m^3; thus, the unfilled foam had lower density than the filled foam samples. At 5wt% filler load, both fillers seem to have the same effect as depicted by the error bars shown on the chart (Figure 4.8). However, the mineral calcium carbonate ($CaCO_3$) filled foam samples were higher than those of eggshell filled foams, with the highest being mineral calcium carbonate at 15wt% composition with a value of 23.77kg/m^3 followed by the 45µm-sized eggshell filled foam with density mean value of 23.53 kg/m^3, standard error of 0.2906 and standard deviation of 0.5033. This implies that, fillers increase density of polyurethane foam. The density of filled foams according to ASTM D 3574 is expected increase with increase in percentage filler composition (Makanjuola, 1999). The result indicated that unfilled foam has lower density than all the filled foams. This could be due to filler particles filling the voids in the polyurethane foam structure which tend to compact the material, thereby reducing the foam's porosity and making it denser. Similarly, Onuegbo, (2012) in the study of the effect coconut and palm kernel shells on density, porosity index and tensile properties of flexible polyether foam had reported that the higher the filler load, the higher the density of the foam.

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4.8 Foam Microstructure

Plates 3 - 7: show the Scanning Electron Microphotograph (SEM) (mag- ×200, Phenom Pro-X) images of the foam samples produced and present the SEM analysis of the flexible polyurethane foams containing 5 w% of egg shell and calcium carbonate.

Based on the SEM micrographs, the flexible (PU) foam composites are found on having open cells cellular structures. By comparing the cellular structures of all the foam composites, larger cells were found on pure (control) PU foams' structure no matter it is observed in surface perpendicular or parallel to the foam direction.

Again, it is observed that the fillers added were agglomerated in some points in the polymer matrix and not evenly distributed homogenously as is required to promote an efficient reinforcement. Even though the use of excessive quantities of filler causes enrichment, it also can be responsible for damage to the matrix (Plate 4.1 – 4.5), causing the foam to lose its characteristic polyhedral morphology.The arrows show the worsening morphology as higher concentrations are added. The same was observed by Singh *et al.*, (200[2])

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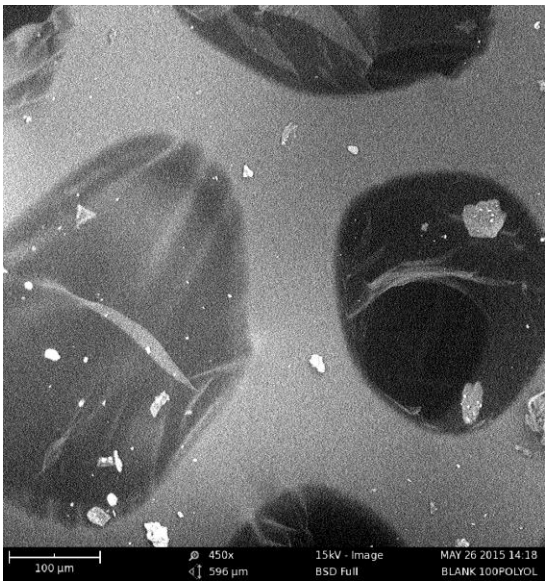


Plate 4.1:100% polyol content

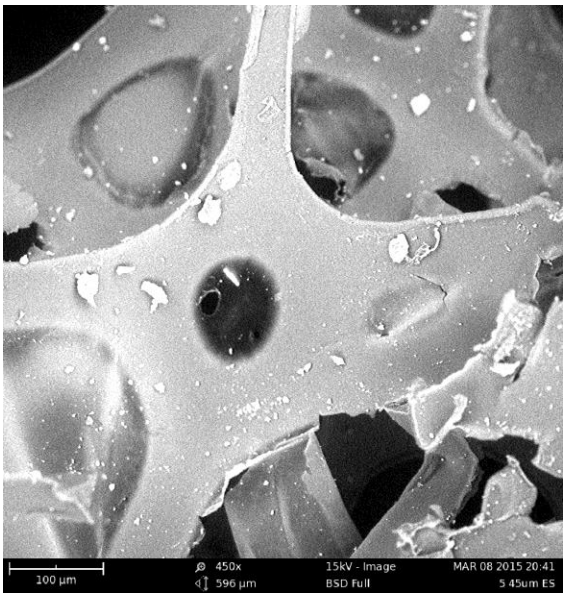


Plate 4.2: 5wt% 45µm ES content



Plate 4.3: 5wt% 63µm ES content

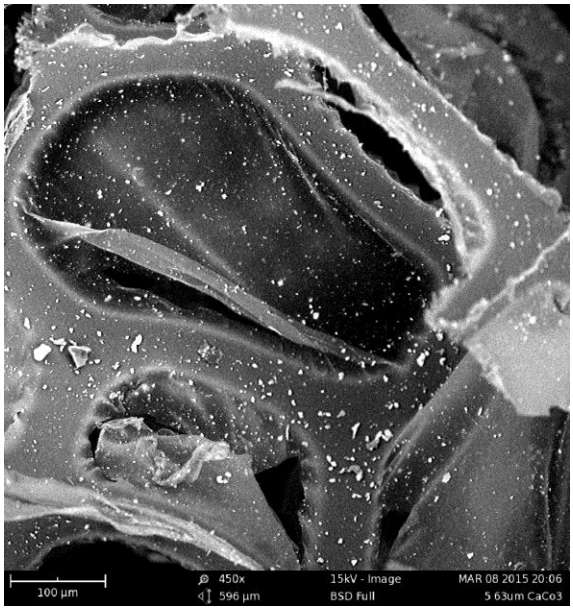


Plate 4.4: 5wt% 63µm $CaCO_3$ content

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Plate 4.5: 5 wt% 90µm ES content

However, all the foam samples show anistropic, though the openness in cell structure of some is more uniform than others. It was reported that, almost all man – made foams are anistropicChan et al., (2012).

Based on the SEM analysis, the flexible polyurethane foam composites are found having open cell cellular structures. The control foam sample was found to have uniform and wide cell structure. However, addition of filler seems to distort the cell arrangement as shown in Plates 4.4, 4.5, 4.5 and 4.6 for both fillers. Based on the SEM, breakages and discontinuity in cell structure were also observed with the filled foam sample micrographs. This could explain the

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reason for the unfilled foam samples displaying better result on most of the mechanical properties than the filled foams. The mechanical properties determined for the filled foam were mostly lower which is expected as reported by Ganiyu *et al.,* (2010), that mechanical properties determined was low indicating that filler addition work negatively to destroy some of the foams mechanical properties.

Furthermore, the cell opening was observed to be wide which represent the space where the CO_2 gas was released during the polymerization reaction. Addition of filler in flexible polyurethane foams (Plates4.3 – 4.6) creates a filler/polymer interface unto which gasses are trapped. It can be observed from Plates 4.4, 4.5,4.6 and 4.7, that there was discontinuity polymer network. In overall, the results of morphology study indicated that fillers tend to modify the microstructure of PU foam to become smaller cell size and thus higher cell density. Similar observations were found on literatures also Verdejo *et al.,* (2009) and Xin *et al.,* (2010). Therefore, the morphology studied agreed with fillers mayserve as nucleating agent that promote the cell nucleation. Which resulting a higher cell density at the final formed (Xin *et al.,* 2010).

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CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

In this chapter, the conclusion and recommendations drawn from the work are presented.

5.1 Conclusions

1. Eggshell of different particle size distribution and loading was successfully used as filler in the production of flexible polyurethane.
2. Beneficiated eggshell was found to contain 1.36 % calcium carbonate in the form of CaO higher than the raw eggshell as revealed by the results of the XRF technique.
3. The compression set of flexible polyurethane foams increased with filler contents for both fillers and particle size in case of eggshell filled foams.
4. The hardness index, support factor and density of the flexible polyurethane composites were found to increase with increase in filler contents and decrease in filler particle size except compression set.
5. The results of the effects of the fillers used on the flexible polyurethane foam samples show that the reinforcing effects of these fillers is more with egg-shells which produced samples with lower compression set and higher support factor, tensile and elongation properties.
6. Unfilled foam sample had the best result of compression set, elongation at break, tensile strength and the heat ageing elongation and tensile properties compared to the filled foams as confirmed by the SEM results.

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7. Improve properties was achieved with lower particle size and higher filler content. The smallness of the particle size provides a larger surface area and hence a large filler-polymer- interaction, with 45μm particle size filled foam samples at 5 wt% filler content had the best effect on most of the mechanical properties of polyurethane foams

5.2 Recommendations

1. Modeling and optimization be conducted so as to know the best operating conditions for eggshell filled foam production.

2. Surface treatment on eggshell particles is needed to improve in its performance as filler on the flexible polyurethane foam.

3. More researches should be conducted on viability and feasibility of other locally available raw materials especially those of organic source such as fish bone, groundnut shell and rice husk etc., on polyurethane foam.

4. Oil from organic source especially the non edible ones can also be investigated to see their suitability as well as potentiality in the synthesis of polyurethane foam.

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APPENDIX A

Calculation of Compression Set

Sample dimension = l × b × h (50mm × 50mm × 25mm)

Compression time = 22 hrs

Compression at ambient temperature = $27^{o}C$

Time of recovery = 30 sec.

Reduction in height (loss of thickness), h

For 100% Polyol content (Pure) sample

$h = t_o - t_f$

Where,

t_o = initial thickness

t_f = final thickness

Sample 1

t_o= 25mm

t_f= 24.4mm

h = (25 – 24.4)

= 0.6

Compression set, % = 0.6/25 × 100

= 2.4 %

Sample 2

t_o= 25mm

t_f= 24.5mm

h = (25 – 24.5)

=0.5

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Compression set, % = 0.5/25 × 100

= 2.0%

Sample 3

t_o= 25mm

t_f= 24.4mm

h = (25 – 24.3)

= 0.7

Compression set, % = 0.7/25 × 100

= 2.8%

Average compression set = 2.4+2.0+2.4/3

= 2.4%

Similarly, other values were calculated and recorded in Tables A1 – A4.

Table A.1 Determination of Compression set and Statistical analysis of 45µm ES filled Flexible Polyurethane Foam

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Compression set, %

Descriptive statistics

Composition	45µm ES Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	2.8	3.6	2.0	8.4	2.80	0.4619	0.8000	0.640
7.5 wt%	3.2	3.6	3.2	10.0	3.33	0.1333	0.2309	0.053
10 wt%	3.6	3.6	3.6	10.8	3.60	0.0000	0.0000	0.000
12.5 wt%	4.0	4.0	4.0	12.0	4.00	0.0000	0.0000	0.000
15 wt%	3.6	4.4	4.8	12.8	4.27	0.3528	0.6110	0.373
100% Polyol	2.4	2.0	2.8	7.2	2.40	0.2309	0.4000	0.160

ES = Eggshell

Table A.2 Determination of Compression set and Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

Compression set, %

Descriptive statistics

`

Composition	63 µm ES Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	3.2	4.0	2.4	9.6	3.20	0.4619	0.8000	0.640
7.5 wt%	3.6	3.2	3.6	10.4	3.47	0.1333	0.2309	0.053
10 wt%	3.6	4.0	4.0	11.6	3.87	0.1333	0.2309	0.053
12.5 wt%	4.4	4.4	4.8	13.6	4.53	0.1333	0.2309	0.053
15 wt%	4.8	4.8	4.8	14.4	4.80	0.0000	0.0000	0.000
100% Polyol	2.4	2.0	2.8	7.2	2.40	0.2309	0.4000	0.160

ES = Eggshell

Table A.3 Determination of Compression set and Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Compression set, %

Descriptive statistics

`

Composition	90 µm ES Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	4.0	3.6	4.4	12.0	4.00	0.2309	0.4000	0.160
7.5 wt%	4.4	4.4	4.4	13.2	4.40	0.0000	0.0000	0.000
10 wt%	4.8	4.4	4.8	14.0	4.67	0.1333	0.2309	0.053
12.5 wt%	4.8	5.2	5.6	15.6	5.20	0.2309	0.4000	0.160
15 wt%	5.2	5.6	5.6	16.4	5.47	0.1333	0.2309	0.053
100% Polyol	2.4	2.0	2.8	7.2	2.40	0.2309	0.4000	0.160

ES = Eggshell

Table A.4 Determination of Compression set and Statistical analysis of 63µm MCC filled Flexible Polyurethane Foam

Compression set, %

Descriptive statistics

Composition	63µm MCC Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	3.3	3.4	3.2	9,9	3.30	0.0577	0.1000	0.010
7.5 wt%	3.4	3.4	4.3	11.1	3.70	0.3000	0.5196	0.270
10 wt%	4.1	4.1	3.8	12.0	4.00	0.1000	0.1732	0.030
12.5 wt%	4.1	4.3	4.5	12.9	4.30	0.1155	0.2000	0.040
15 wt%	4.4	4.3	4.8	13.5	4.50	0.1528	0.2646	0.070
100% Polyol	2.4	2.0	2.8	7.2	2.40	0.2309	0.4000	0.160

CC = Mineral calcium carbonate

APPENDIX B

Determination of Foam Hardness

Table B.1 Determination of Hardness Index of 45µm ES Flexible Polyurethane Foam

Hardness index, N

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	Composition					
Indentation	100% Polyol	5 wt%	7.5 wt%	10 wt%	12.5 wt%	15 wt%
75/25	136.03	139.40	141.11	142.66	144.56	146.71
	136.00	139.11	141.00	142.60	144.31	146.41
	136.00	139.10	141.20	142.50	144.00	146.40
60/40	101.50	100.1	96.20	95.50	96.10	98.10
	103.30	95.30	95.00	93.10	95.71	97.50
	101.10	98.10	95.60	96.00	94.86	97.20
35/65	67.03	50.51	49.00	49.00	49.00	48.90
	66.02	49.16	48.62	48.67	48.60	48.90
	66.03	49.15	48.64	48.64	48.65	47.23

ES = Eggshell

Table B.2 Determination of Hardness Index of 63µm MCC filled Flexible Polyurethane Foam

Hardness index, N						
	Composition					

`

Indentation	100% Polyol	5 wt%	7.5 wt%	10 wt%	12.5 wt%	15 wt%
75/25	136.03	138.40	139.50	142.22	143.00	145.60
	136.00	138.60	141.00	142.20	143.00	145.30
	136.00	138.30	140.00	142.70	143.00	145.10
60/40	101.50	96.33	97.10	97.45	97.50	97.92
	103.30	95.00	96.91	98.21	97.60	98.10
	101.10	95.71	96.55	98.10	97.70	98.15
35/65	67.03	51.64	51.48	52.29	51.63	52.00
	66.02	53.31	52.22	52.00	51.44	51.34
	66.03	52.59	52.00	52.66	50.89	51.45

ES = Eggshell

Table B.3 Determination of Hardness Index of 90µm ES Flexible Polyurethane Foam

Hardness index, N	
Composition	

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Indentation	100% Polyol	5 wt%	7.5 wt%	10 wt%	12.5 wt%	15 wt%
75/25	136.03	136.30	140.00	141.50	142.33	145.00
	136.00	136.00	140.00	141.20	143.10	144.40
	136.00	136.23	140.00	141.00	142.10	144.80
60/40	101.50	94.88	97.30	98.34	96.70	93.79
	103.30	95.00	91.50	97.51	96.50	95.31
	101.10	94.37	93.10	96.50	96.40	95.49
35/65	67.03	53.45	54.10	54.00	53.70	53.11
	66.02	54.40	53.64	53.69	55.04	53.48
	66.03	53.00	53.85	53.41	52.81	53.43

ES = Eggshell

Table B.4 Determination of Hardness Index of 63µm MCC Flexible Polyurethane Foam

Hardness index, N	
Composition	

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Indentation	100% Polyol	5 wt%	7.5 wt%	10 wt%	12.5 wt%	15 wt%
75/25	136.03	146.30	148.40	150.00	152.00	153.00
	136.00	146.80	148.20	150.00	152.60	153.30
	136.00	146.70	148.00	149.60	152.10	153.00
60/40	101.50	100.00	100.70	101.50	102.50	101.67
	103.30	100.40	100.21	101.60	102.50	102.50
	101.10	100.50	99.61	101.00	102.30	102.20
35/65	67.03	53.20	52.44	52.45	52.06	51.17
	66.02	54.57	52.00	51.90	52.08	51.10
	66.03	53.93	52.11	51.41	51.39	46.08

CC = Mineral calcium carbonate

Table B.5 Descriptive Statistics of Hardness Index of 45µm ES filled Flexible Polyurethane Foam

Hardness index, N

Descriptive statistics

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Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	139.4	139.1	139.1	417.6	139.20	0.9838	0.17039	0.029
7.5 wt%	141.1	141.2	141.2	423.3	141.10	0.5783	0.10017	0.010
10 wt%	142.7	142.5	142.5	428.2	142.72	0.14742	0.25534	0.065
12.5 wt%	143.9	144.0	144.0	431.9	143.97	0.03333	0.05774	0.003
15 wt%	146.7	145.3	145.3	438.4	146.15	0.41802	0.05774	0.524
100% Polyol	136.0	136.0	136.1	408.1	136.03	0.01732	0.03000	0.001

ES = Eggshell

Table B.6 Descriptive Statistics of Hardness Index of 63µm ES filled Flexible Polyurethane Foam

Hardness index, N

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	133.1	132.6	133.3	399.0	132.99	0.20537	0.35572	0.127
7.5 wt%	135.2	134.3	133.1	402.6	134.19	0.59229	1.02588	1.052
10 wt%	139.0	140.2	140.1	419.3	139.78	0.39209	0.67912	0.461
12.5 wt%	141.1	143.2	141.6	426.0	141.98	0.63144	1.09368	1.196
15 wt%	144.5	144.2	145.0	433.7	144.55	0.24906	0.43139	0.186
100% Polyol	136.0	136.0	136.1	408.1	136.03	0.01732	0.03000	0.001

ES = Eggshell

Table B.7 Descriptive Statistics of Hardness Index of 90µm ES filled Flexible Polyurethane Foam

Hardness index, N

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	130.5	130.3	130.2	391.0	130.32	0.10088	0.45044	0.031
7.5 wt%	133.6	134.0	133.5	401.1	133.70	0.15275	0.96437	0.070
10 wt%	139.6	136.0	136.5	412.1	137.37	1.12926	1.95594	3.826
12.5 wt%	138.5	137.9	138.0	414.4	138.15	0.19342	0.33501	0.112
15 wt%	140.0	140.1	140.4	420.5	140.17	0.11930	0.20664	0.043
100% Polyol	136.0	136.0	136.1	408.1	136.03	0.01732	0.03000	0.001

ES = Eggshell

Table B.8 Descriptive Statistics of Hardness Index of 63µm MCC filled Flexible Polyurethane Foam

Hardness index

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	146.4	143.5	145.8	435.6	97.58	0.26006	0.45044	0.203
7.5 wt%	147.6	148.4	148.1	444.2	95.40	0.55678	0.96437	0.930
10 wt%	149.0	151.1	150.0	450.1	93.90	0.36056	0.62450	0.390
12.5 wt%	152.6	153.0	152.0	457.6	90.98	0.24504	0.42442	0.180
15 wt%	153.0	155.0	156.0	464.0	88.07	0.88380	1.53080	2.343
100% Polyol	136.0	136.0	136.1	408.1	136.0	0.01732	0.03000	0.001

CC = Mineral calcium carbonate

APPENDIX C

Calculation of Elongation at Break

Elongation at break = Change in gauge length expressed as a percentage of original length, determined at the time of break.

$E = L_1 - L_o / L_1 \times 100$

Where,

L_o = original length

L_1 = final length

The initial gauge length, L_o = 100mm

For 100% polyols content (unfilled) foam sample

`

Sample 1

L_1 = 253mm

ε = (253 – 100)/100

= (153/100) × 100

=153.00%

Sample 2

L_1 = 253.8mm

ε = 153.80%

Sample 3

L_1 = 252.9mm

ε = 152.9%

Average EAB = (153+153.8+152.9)/3

= 459.7/3

= 153.2333333

= 153.23%

Similarly, other values were calculated and recorded in Tables C1 – C4.

Table C.1 Determination of Elongation at breakand Statistical analysis of 45µm ES filled Flexible Polyurethane Foam

Elongation at break, %						
		Descriptive statistics				
Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	151.4	151.0	150.2	452.6	150.87	0.3528	0.6110	0.373
7.5 wt%	145.7	144.1	147.5	437.3	145.77	0.9821	1.7010	2.893
10 wt%	141,5	142.0	140.9	424.4	141.47	0.3180	0.5508	0.303
12.5 wt%	140.0	137.3	138.7	416.0	138.67	0.7796	1.3503	1.823
15 wt%	132.8	136.6	135.0	404.4	134.80	1.1015	1.9079	3.640
100% Polyol	153.0	153.6	152.9	459.5	153.17	0.2186	0.3786	0.143

ES = Eggshell

Table C.2 Determination of Elongation at breakand Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

Elongation at break, %

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	148.6	142.2	148.3	439.1	146.37	2.0851	3.6116	13.043
7.5 wt%	143.3	143.1	143.0	429.4	143.13	0.0882	0.1528	0.023
10 wt%	140,0	141.0	139.8	420.8	140.27	0.3712	0.6429	0.413
12.5 wt%	136.4	136.0	140.0	412.4	137.47	1.2719	2.2030	4.853
15 wt%	134.1	134.4	132.8	401.3	133.77	0.4910	0.8505	0.723
100% Polyol	153.0	153.6	152.9	459.5	153.17	0.2186	0.3786	0.143

ES = Eggshell

`

Table C.3 Determination of Elongation at break and Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Elongation at break, %

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5wt%	142.3	143.4	142.8	428.5	142.83	0.3180	0.5508	0.303
7.5 wt%	140.9	141.0	140.0	421.9	140.63	0.3180	0.5508	0.303
10 wt%	137.0	137.3	137.1	411.4	137.13	0.0882	0.1528	0.023
12.5 wt%	134.6	136.1	137.7	408.4	136.13	0.8950	1.5503	2.403
15 wt%	130.5	134.6	133.3	398.4	132.80	1.2097	2.0952	4.390
100% Polyol	153.0	153.6	152.9	459.5	153.17	0.2186	0.3786	0.143

ES = Eggshell

`

Table C.4 Determination of Elongation at break and Statistical analysis of 63µm MCC filled Flexible Polyurethane Foam

Elongation at break, %

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	145.6	146.3	144.1	436.0	145.33	0.6489	1.1240	1.263
7.5 wt%	143.3	143.8	144.0	431.1	143.70	0.2082	0.3606	0.130
10 wt%	140.5	141.5	141.2	423.2	141.07	0.2963	0.5132	0.263
12.5 wt%	136.8	139.1	141.0	416.9	138.97	1.2143	2.1032	4.423
15 wt%	136.3	135.7	136.4	408.4	136.13	0.2186	0.3786	0.143
100% Polyol	153.0	153.6	152.9	459.5	153.17	0.2186	0.3786	0.143

CC = Mineral calcium carbonate

APPENDIX D

`

Calculation of Tensile Strength

Is the stress at the breaking point of a specimen expressed in kN/m^2 .It is also, the maximum force required to break a test-piece, divided by its original cross-sectional area.

Tensile strength = Stress/Strain

Stress, $\sigma = P/A$

Strain, $\varepsilon = \Delta L/L_o = L - L_o/L_o$

For 100% polyols content (unfilled) foam sample

Sample 1

$L_o = 100mm = 0.1m$

$L = 253mm = 0.253m$

$\varepsilon = (253 - 100)/100$

$= 1.53$

$P = 29330.1N = 29.3301kN$

$A = width \times height\ (thickness)$

$Width, w = 60mm = 0.06m$

$Thickness, t = 3mm = 0.003$

$Cross\text{-}sectional\ area, csa\ (A_o) = 0.06 \times 0.003$

$= 0.18m^2$

$\sigma = 29.3301/0.18$

$= 162.945kN/m^2$

$Tensile\ strength, E = 162.945/1.53$

$= 106.5kN/m^2$

`

Sample 2

L_o = 100mm = 0.1m

L = 253.2mm = 0.2532m

ε = (253.2 – 100)/100

= 1.532

P = 29258.136N = 29.258136kN

A = width × height (thickness)

Width, w = 60mm = 0.06m

Thickness, t = 3mm = 0.003

Cross-sectional area, csa (A_o) = 0.06 × 0.003

= $0.18m^2$

σ = 29.3301/0.18

= $162.54k52N/m^2$

Tensile strength, E = 162.945/1.532

= $106.1kN/m^2$

Sample 3

L_o = 100mm = 0.1m

L = 252.9mm = 0.2529m

ε = (252.9 – 100)/100

= 1.529

P = 27604.566N = 27.604566kN

A = width × height (thickness)

Width, w = 60mm = 0.06m

Thickness, t = 3mm = 0.003

`

Cross-sectional area, csa (A_o) = 0.06 × 0.003

$= 0.18m^2$

$\sigma = 27.604566/0.18$

$= 153.3587kN/m^2$

Tensile strength, E = 153.358/1.529

$= 100.3kN/m^2$

Average tensile strength = (106.5 + 106.1 + 100.3)/3

= 312.9/3

= 104.300

$= \underline{104.3kN/m^2}$

Similarly, other values were calculated and recorded in Tables D1 – D4.

Table D.1 Determination of Tensile strength and Statistical analysis of 45µm ES filled Flexible Polyurethane Foam

Tensile strength, kN/m^2
Descriptive statistics

`

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	100.1	99.6	98.4	298.1	99.37	0.5044	0.8737	0.763
7.5 wt%	100.0	96.5	98.7	295.2	98.40	1.0214	1.7692	3.130
10 wt%	97.1	96.0	94.2	287.3	95.77	0.8452	1.4640	2.143
12.5 wt%	96.6	92.8	95.0	284.4	94.80	1.1015	1.9079	3.640
15 wt%	93.7	90.5	91.1	275.3	91.77	0.9821	1.7010	2.893
100% Polyol	106.5	106.1	100.3	312.9	104.30	2.0033	3.4699	12.040

ES = Eggshell

Table D.2 Determination of Tensile strength and Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

Tensile strength, kN/m^2

Descriptive statistics

`

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	98.1	97.3	98.4	293.8	97.93	0.3283	0.5686	0.323
7.5 wt%	96.7	97.0	97.5	291.2	97.07	0.2333	0.4041	0.163
10 wt%	94.9	96.8	95.5	287.2	95.73	0.5608	0.9713	0.943
12.5 wt%	90.5	93.4	95.0	278.9	92.97	1.3170	2.2811	5.203
15 wt%	90.1	91.3	89.6	271.0	90.33	0.5044	0.8737	0.763
100% Polyol	106.5	106.1	100.3	312.9	104.30	2.0033	3.4699	12.040

ES = Eggshell

Table D.3 Determination of Tensile strength and Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Tensile strength, kN/m^2

Descriptive statistics

`

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	99.3	97.3	98.2	294.8	98.27	0.5783	1.0017	1.003
7.5 wt%	95.1	96.7	98.2	290.0	96.67	0.8950	1.5503	2.403
10 wt%	95.3	95.1	93.8	284.2	94.73	0.4702	0.8145	0.663
12.5 wt%	92.3	93.3	92.8	278.4	92.80	0.2887	0.5000	0.250
15 wt%	90.5	90.3	88.9	269.7	89.90	0.5033	0.8718	0.760
100% Polyol	106.5	106.1	100.3	312.9	104.30	2.0033	3.4699	12.040

ES = Eggshell

Table D.4 Determination of Tensile strength and Statistical analysis of 63µm MCC filled Flexible Polyurethane Foam

Tensile strength, kN/m^2

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	95.3	94.2	96.3	285.8	95.27	0.6064	1.0504	1.103
7.5 wt%	92.4	93.1	93.0	278.5	92.83	0.2186	0.3786	0.143
10 wt%	90.1	93.0	90.0	273.1	91.03	0.9838	1.7039	2.903
12.5 wt%	89.0	89.1	87.5	265.6	88.53	0.5175	0.8963	0.803
15 wt%	84.4	87.0	83.4	254.8	84.93	1.0729	1.8583	3.453
100% Polyol	106.5	106.1	100.3	312.9	104.30	2.0033	3.4699	12.040

CC = Mineral calcium carbonate

APPENDIX E

Calculation of Elongation at Break after Heat Ageing

Elongation at break = Change in gauge length expressed as a percentage of original length, determined at the time of break.

Temperature, T = 140^{o}C

Time, t = 16hrs

$E = L_1 - L_o / L_1 \times 100$

`

Where,

L_o = original length

L_1 = final length

The initial gauge length, L_o = 100mm

For 100% polyols content (unfilled) foam sample

Sample 1

L_1 = 254.16mm

ε = (254.16 – 100)/100

= (154.16/100) × 100

=154.16%

Sample 2

L_1 = 254.06mm

ε = 154.06%

Sample 3

L_1 = 253.13mm

ε = 153.13%

Average EAB = (154.16+154.06+154.13)/3
= 459.7/3
= 154.1166666667
= 154.17%

Similarly, other values were calculated and recorded in Tables E.1 – E.4.

Table E.1 Determination of Heat Elongation at break and Statistical analysis of 45µm ES filled Flexible Polyurethane Foam

Heat Ageing Elongation at break, %						
		Descriptive statistics				
Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	152.1	153.0	151.3	456.4	152.14	0.51052	0.88425	0.782
7.5 wt%	147.1	145.3	157.5	439.9	146.63	0.73106	1.26623	1.603
10 wt%	143.0	143.6	141.4	428.1	142.70	0.75596	1.30936	1.714
12.5 wt%	141.7	140.0	140.2	421.9	140.63	1.87021	3.23930	10.493
15 wt%	136.1	138.2	136.7	411.0	137.00	2.13938	3.70551	13.731
100% Polyol	154.2	154.1	153.1	461.4	153.78	0.32794	\0.56801	0.323

ES = Eggshell

Table E.2 Determination of Heat Elongation at break and Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

Heat Ageing Elongation at break, %

		Descriptive statistics				
Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	145.6	144.1	144.0	433.7	144.57	0.51052	0.88425	0.782
7.5 wt%	140.7	143.1	141.2	425.0	141.67	0.73106	1.26623	1.603
10 wt%	139.6	138.5	141.1	419.2	139.73	0.75596	1.30936	1.714
12.5 wt%	133.1	139.1	138.2	410.5	136.83	1.87021	3.23930	10.493
15 wt%	126.8	130.2	134.2	391.2	130.4	2.13938	3.70551	13.731
100% Polyol	154.2	154.1	153.1	461.4	153.78	0.32794	0.56801	0.323

ES = Eggshell

`

Table E.3 Determination of Heat Elongation at breakand Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Heat Elongation at break, %

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	134.2	137.6	136.6	408.4	136.14	1.00489	1.74053	3.029
7.5 wt%	133.8	134.0	130.7	398.5	132.82	1.08639	1.88167	3.541
10 wt%	130.3	130.6	132.1	393.1	131.03	0.54931	0.95144	0.905
12.5 wt%	128.2	129.0	128.0	385.2	128.40	0.32126	0.55645	0.310
15 wt%	123.6	122.0	124.6	370.2	123.40	0.75719	1.31149	1.720
100% Polyol	154.2	154.1	153.1	461.4	153.78	0.32794	0.56801	0.323

ES = Eggshell

`

Table E.4 Determination of Heat Elongation at breakand Statistical analysis of 63µm MCC filled Flexible Polyurethane Foam

Heat Elongation at break, %

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt %	144.1	143.9	143.2	431.3	143.76	0.26535	0.45960	0.211
7.5 wt %	142.6	142.3	140.0	424.9	141.62	0.81296	1.40808	1.983
10 wt %	136.7	137.1	140.1	413.9	137.97	1.07290	1.85831	3.453
12.5 wt %	138.1	135.6	135.5	409.2	136.40	0.84873	1.47005	2.161
15 wt %	126.4	131.1	129.0	386.5	128.83	1.35933	2.35443	5.543
100% Polyol	154.2	154.1	153.1	461.4	153.78	0.32794	0.56801	0.323

CC = Mineral calcium carbonate

`

APPENDIX F

Calculation Tensile Strength after Heat Ageing

Is the stress at the breaking point of a specimen expressed in kN/m^2 .It is also, the maximum force required to break a test-piece, divided by its original cross-sectional area.

Tensile strength = Stress/Strain
Temperature, T = 140^oC

Time, t = 16hrs

Stress, $\sigma = P/A_o$

Strain, $\varepsilon = \Delta L/L_o = L - L_o/L_o$

For 100% polyols content (unfilled) foam sample

L_o = 100mm = 0.1m

L = 254.16mm = 0.25416m

ε = (254.16 – 100)/100

= 1.5416

P = 32826.8304N = 32.8268304kN

A = width × height (thickness)

Width, w = 60mm = 0.06m

Thickness, t = 3mm = 0.003

Cross-sectional area, csa (A_o) = 0.06 × 0.003

$= 0.18m^2$

$\sigma = 32.8268304/0.18$

$= 182.37128kN/m^2$

Tensile strength, E = 182.37128/1.5416

$= 118.3kN/m^2$

`

Sample 2

L_o = 100mm = 0.1m

L = 254.06mm = 0.25406m

ε = (254.06 – 100)/100

= 1.5406

P = 32694.6132N = 32.6946132kN

A = width × height (thickness)

Width, w = 60mm = 0.06m

Thickness, t = 3mm = 0.003

Cross-sectional area, csa (A_o) = 0.06 × 0.003

= $0.18m^2$

σ = 32.6946132/0.18

= $181.63674N/m^2$

Tensile strength, E = 181.63674/1.5406

= $117.9kN/m^2$

Sample 3

L_o = 100mm = 0.1m

L = 253.13mm = 0.25313m

ε = (253.13 – 100)/100

= 1.5313

P = 33103.6434N = 33.1036434kN

A = width × height (thickness)

Width, w = 60mm = 0.06m

Thickness, t = 3mm = 0.003

`

Cross-sectional area, csa (A_o) = 0.06 × 0.003

= $0.18m^2$

σ = 33.1036434/0.18

= $183.90913kN/m^2$

Tensile strength, E = 183.90913/1.5313

= $120.1kN/m^2$

Average tensile strength = (118.3 + 117.9 + 120.1)/3

= 356.3/3

= 118.7666667

= $\underline{118.77kN/m^2}$

Similarly, other values were calculated and recorded in Tables F.1 – F.4.

Table F.1 Determination of Heat Tensile strengthand Statistical analysis of 45μm ES filled Flexible Polyurethane Foam

Heat Ageing Tensile strength, kN/m^2

`

Descriptive statistics							
Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt %	106.6	99.6	99.1	305.3	101.78	2.42064	4.19266	17.578
7.5 wt %	98.5	99.0	98.7	296.7	98.9 0	0.13618	0.23587	0.056
10 wt %	96.6	95.8	96.1	288.5	96.17	0.13618	0.40336	0.163
12.5 wt %	95.1	96.3	95.5	286.9	95.63	0.23288	0.61101	0.373
15 wt %	91.1	90.6	90.7	272.4	90.80	0.35277	0.27221	0.740
100% Polyol	118.3	117.9	120.1	461.4	153.78	0.32794	0.56801	0.323

ES = Eggshell

Table F.2 Determination of Heat Tensile strength and Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

Heat Ageing Tensile strength, kN/m^2

Descriptive statistics

`

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	100.3	99.6	99.5	299.4	99.80	0.25166	0.43589	0.190
7.5 wt%	96.7	97.0	98.2	291.9	97.31	0.46808	0.81074	0.657
10 wt%	95.5	94.7	95.0	285.2	95.07	0.23333	0.40415	0.163
12.5 wt%	93.4	95.0	93.2	281.6	93.85	0.57823	1.00152	1.003
15 wt%	92.5	92.1	92.8	277.4	92.47	0.20276	0.35119	0.123
100% Polyol	118.3	117.9	120.1	461.4	153.78	0.32794	0.56801	0.323

ES = Eggshell

Table F.3 Determination of Heat Elongation at breakand Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Heat Ageing Tensile strength, kN/m^2

Descriptive statistics

Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	101.3	100.0	98.7	300.0	100.00	0.75056	1.30000	1.690
7.5 wt%	97.4	99.3	98.5	295.2	98.40	0.55076	0.95394	0.910
10 wt%	95.6	98.1	96.0	289.7	96.57	0.77531	1.34288	1.803
12.5 wt%	94.4	94.3	94.3	283.0	94.33	0.03333	0.05774	0.003
15 wt%	91.2	90.7	90.1	272.0	90.68	0.31540	0.54629	0.298
100% Polyol	118.3	117.9	120.1	461.4	153.78	0.32794	0.56801	0.323

ES = Eggshell

Table F.4 Determination of Heat Tensile strengthand Statistical analysis of 63µm MCC filled Flexible Polyurethane Foam

Heat Ageing Tensile strength, kN/m^2

		Descriptive statistics				
Composition	Sample	Sum	Mean	Std. Error	Std. Dev.	Variance

`

5 wt%	97.33	98.1	97.3	292.7	97.58	0.26006	0.45044	0.203
7.5 wt%	96.5	94.7	95.0	286.2	95.40	0.55678	0.96437	0.930
10 wt%	93.2	94.1	94.4	281.7	93.90	0.36056	0.62450	0.390
12.5 wt%	90.5	91.1	91.3	273.0	90.98	0.24504	0.42442	0.180
15 wt%	89.0	88.9	86.3	264.2	88.07	0.88380	1.53080	2.343
100% Polyol	118.3	117.9	120.1	461.4	153.78	0.32794	0.56801	0.323

CC = Mineral calcium carbonate

`

APPENDIX G

Calculation of Support Factor

The support factor was calculated using standard formula:

S.F = 75% Indentation /35% Indentation

For 100% Polyol foam samples

Sample 1

S.F = 136.03/67.03

= 2.76

Sample 2

S.F = 136.00/66.02

= 2.78

Sample 3

S.F = 136.60/66.03

= 2.78

Average S.F = (2.76 + 2.78 + 2.78)/3

= 8.32/3
= 2.77

Similarly, other values were calculated and recorded in Tables G.1 – G.4.

Table G.1 Determination of Support Factor of 45µm ES Flexible Polyurethane Foam

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Support factor

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	2.76	2.78	2.78	8.32	2.77	0.00667	0.01155	0.000
7.5 wt%	2.89	2.93	2.94	8.76	2.92	0.01528	0.02646	0.001
10 wt%	2.91	2.98	2.99	8.56	2.85	0.13170	0.22811	0.052
12.5 wt%	2.94	3.12	3.12	9.18	3.06	0.06000	0.10392	0.011
15 wt%	3.18	3.24	3.36	9.78	3.26	0.05292	0.9165	0.008
100% Polyol	2.03	2.06	2.03	6.12	2.04	0.01000	0.01732	0.000

ES = Eggshell

Table G.2 Determination of Support Factor of 63µm ES Flexible Polyurethane Foam

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Support factor

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	2.63	2.59	2..56	7.78	2.59	0.02028	0.03512	0.001
7.5 wt%	2.63	2.60	2.59	7.82	2.60	0.01202	0.02082	0.000
10 wt%	2.66	2.65	2.70	8.01	2.67	0.01528	0.02646	0.001
12.5 wt%	2.72	2.70	2.71	8.13	2.71	0.00577	0.10000	0.000
15 wt%	2.71	2.72	2.72	8.15	2.72	0.00333	0.00577	0.000
100% Polyol	2.03	2.06	2.03	6.12	2.04	0.01000	0.01732	0.000

ES = Eggshell

Table G.3 Determination of Support Factor of 90µm ES Flexible Polyurethane Foam

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Support factor

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	2.40	2.41	2.40	7.21	2.40	0.00333	0.00577	0.000
7.5 wt%	2.50	2.45	2.43	7.38	2.46	0.02082	0.03606	0.001
10 wt%	2.59	2.40	2.42	7.41	2.47	0.06028	0.10440	0.011
12.5 wt%	2.60	2.51	2.90	8.01	2.67	0.11790	0.20421	0.042
15 wt%	2.99	2.92	2.93	8.84	2.95	0.02186	0.03786	0.001
100% Polyol	2.03	2.06	2.03	6.12	2.04	0.01000	0.01732	0.000

ES = Eggshell

Table G.4 Determination of Support Factor of 63µm MCC Flexible Polyurethane Foam

Support factor

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Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	2.56	2.68	2.75	7.99	2.66	0.05548	0.09609	0.009
7.5 wt%	2.73	2.76	2.76	8.25	2.75	0.01000	0.01732	0.000
10 wt%	2.73	2.78	2.76	8.27	2.76	0.01453	0.12517	0.001
12.5 wt%	2.78	2.80	2.77	8.33	2.78	0.00882	0.01528	0.000
15 wt%	2.85	2.80	2.75	8.43	2.81	0.02646	0.04583	0.002
100% Polyol	2.03	2.06	2.03	6.12	2.04	0.01000	0.01732	0.000

CC = Mineral calcium carbonate

APPENDIX H

Calculation of Density

Sample dimension l×b×h (10×10×5cm)

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Weight in grams (g)

Apparent density = mass/ volume

D = M/V

Conversion of length (cm to m)

10cm = 10/1000m = 0.1m

10cm = 10/1000m = 0.1m

5cm = 5/1000m = 0.05m

v = $0.1 \times 0.1 \times 0.05 = 0.0005m^3$

Conversion of weight, m (g to kg)

For 100% polyols content (unfilled) foam sample

Sample 1

m = 8.75g/1000kg

= 0.00875kg

D = M/V

=0.00875/0.0005

= $\underline{17.5\ kg/m^3}$

Sample 2

M = 8.75g/1000kg

= 0.00875kg

D = M/V

=0.00875/0.0005

= $\underline{17.5\ kg/m^3}$

Sample 3

M = 8.75g/1000kg

= 0.00875kg

D = M/V

=0.00875/0.0005

= $\underline{17.5\ kg/m^3}$

Average density = (17.5+17.5+17.5)/3

= $\underline{17.5kg/m^3}$

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Similarly, other values were calculated and recorded in Tables H1 – H8.

Table H.1 Determination of Density and Statistical analysis of 45µm ES filled Flexible Polyurethane Foam

Density,kg/m^3

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	18.4	18.0	18.5	54.9	18.30	0.1528	0.2646	0.070
7.5 wt%	19.9	20.2	20.0	60.1	20.03	0.0882	0.1528	0.023
10 wt%	20.8	21.2	21.0	63.0	21.00	0.1155	0.2000	0.040
12.5 wt%	21.8	22.0	22.4	66.2	22.07	0.1764	0.3055	0.093
15 wt%	23.0	24.0	23.6	70.6	23.53	0.2906	0.5033	0.253
100% Polyol	17.5	17.7	17.3	52.5	17.50	0.0667	0.1155	0.013

ES = Eggshell

Table H.2 Determination of Density and Statistical analysis of 63µm ES filled Flexible Polyurethane Foam

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Density,kg/m^3

Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	18.0	18.3	18.4	54.7	18.23	0.1202	0.2082	0.043
7.5 wt%	18.6	18.5	19.2	56.3	18.75	0.2270	0.3931	0.155
10 wt%	19.2	19.5	19.6	58.3	19.43	0.1202	0.2082	0.043
12.5 wt%	20.0	20.4	19.0	60.4	20.14	0.1286	0.2228	0.050
15 wt%	21.8	20.4	20.1	64.2	21.40	0.5033	0.8718	0.760
100% Polyol	17.5	17.7	17.3	52.5	17.50	0.0667	0.1155	0.013

ES = Eggshell

Table H.3 Determination of Density and Statistical analysis of 90µm ES filled Flexible Polyurethane Foam

Density,kg/m^3

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Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	17.0	17.4	18.0	52.4	17.48	0.2906	0.2646	0.253
7.5 wt%	17.6	17.8	17.8	53.2	17.73	0.0667	0.1528	0.013
10 wt%	18.0	18.0	18.0	54.0	18.00	0.0000	0.2000	0.000
12.5 wt%	19.0	18.6	20.0	57.6	19.21	0.4116	0.3055	0.508
15 wt%	20.1	20.2	20.2	60.5	20.17	0.0333	0.0577	0.003
100% Polyol	17.5	17.7	17.3	52.5	17.50	0.0667	0.1155	0.013

ES = Eggshell

Table H.4 Determination of Density and Statistical analysis of 45µm CC filled Flexible Polyurethane Foam

Density,kg/m^3

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Descriptive statistics

Composition	Sample			Sum	Mean	Std. Error	Std. Dev.	Variance
5 wt%	19.9	20.6	20.2	60.7	20.23	0.2028	0.3512	0.123
7.5 wt%	20.8	21.0	22.0	63.8	21.27	0.3712	0.6429	0.413
10 wt%	22.0	21.2	22.0	65.2	21.73	0.2667	0.4619	0.213
12.5 wt%	22.2	22.6	22.0	66.8	22.27	0.1764	0.3055	0.093
15 wt%	23.0	24.3	24.0	71.3	23.77	0.3930	0.6807	0.463
100% Polyol	17.5	17.7	17.3	52.5	17.50	0.0667	0.1155	0.013

CC = Mineral calcium carbonate

APPENDIX I

Laboratory Equipment and Sample Photos

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Plate I.1: Flexible Polyurethane Foam Production



Plate I.2: Arrangement of foam sample into compression test device

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Plate I.3: Arrangement of foam sample in indentation (hardness) test machine

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Plate I.4: Arrangement of foam sample in a tensile strength (tension) test machine

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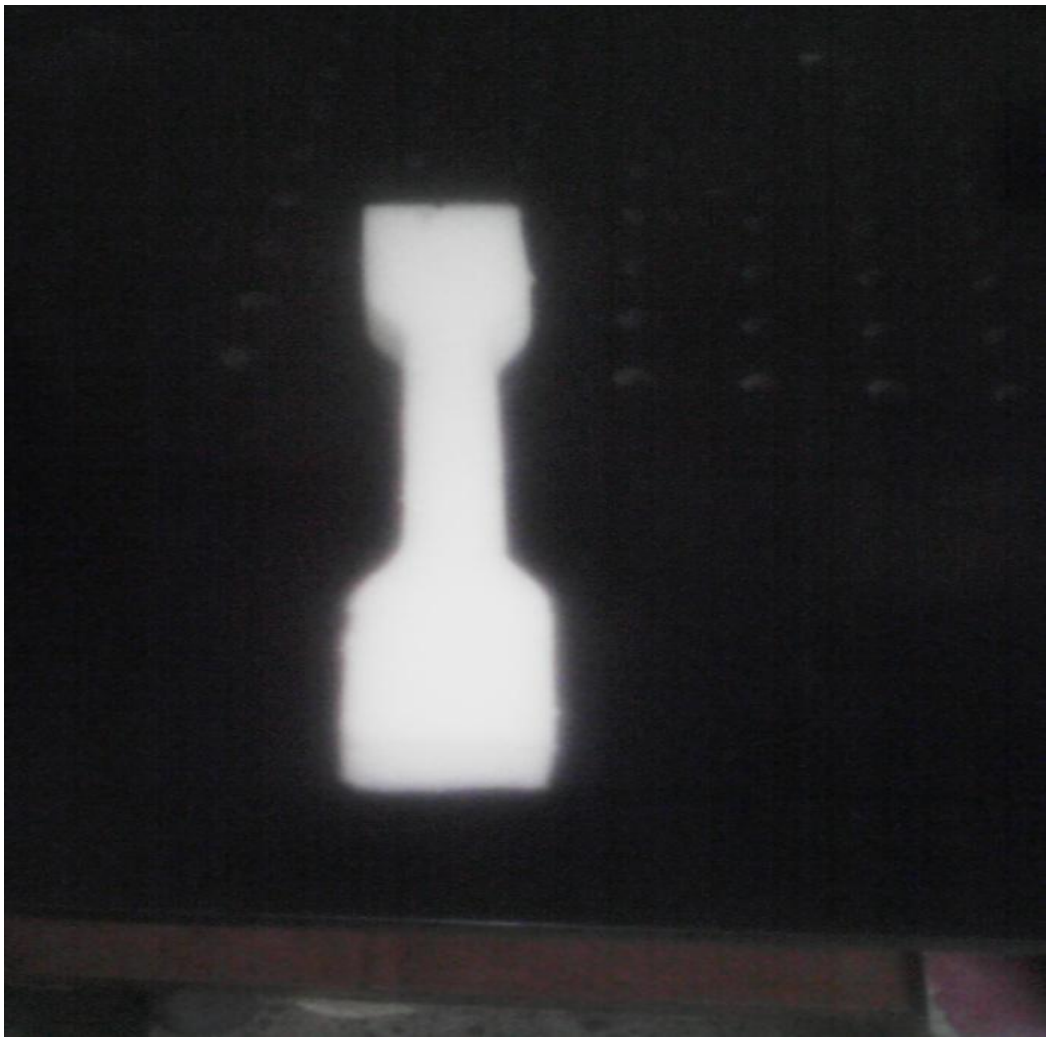


Plate I.5: “Dumb bell or dog bone” shaped foam sample for tensile and elongation tests

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Plate I.6: Arrangement of foam sample on a weighing scale for density test