The Efficacy of *Hibiscus sabdariffa* as a Fibre-Reinforcement Material for Denture Base Acrylic Resins

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Dedication

This study is dedicated to Ebelechukwu, my loving wife, and our children – Chukwuka, Chidumeje and Chidiebube – for your love and endurance.

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Abstract

The poor mechanical properties of denture base acrylic resins can cause dentures to fracture either through impact or stress fatigue. Various metal reinforcing materials such as powders, nets, plates and wires together with synthetic fibres are therefore used to improve the strength properties of denture base acrylic resins. Despite their benefits, they are difficult to apply during fabrication, are costly, non-recyclable, and not environmentally friendly. The suitability of *Hibiscus sabdariffa* (*H. sabdariffa*) as a fibre reinforcement material for denture base acrylic resins was therefore investigated. A quantitative research paradigm and a two-phased experimental research design was used.

The preliminary study used Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and field emission scanning electron microscope (FE-SEM) to assess the characteristics of, and the effect of, mercerisation on *H. sabdariffa* fibres. In determining the suitability of *H. sabdariffa* fibres, fibre diameter, fibre density, moisture content and absorption were examined. The main study investigated the mechanical and physical properties of two sample groups namely: the unreinforced (control) group and the *H. sabdariffa* fibre-reinforced (test) group denture base acrylic resins. The flexural strength, impact strength, specific wear rate, hardness and water absorption behaviour were determined in line with ASTM D 790 and D 256, G 99, D 2583 and D 570 methods of testing, respectively. Parametric and non-parametric tests were used to analyse the mean differences ($p = 0.05$) between the unreinforced and the *H. sabdariffa* fibre-reinforced denture base acrylic resins.

The preliminary study revealed that *H. sabdariffa* fibres favourably compared to other lignocellulosic fibres in terms of fibre diameter, fibre density, water content and absorption behaviour. In the main study, a t-test revealed that there were significant differences in flexural strength at 0^oC ($p < 0.0001$) and at 65^oC ($p < 0.0025$) between the two sample groups. Similarly, there were significant differences in the impact strength between the two sample groups at 0^oC ($p < 0.031$) and at 65^oC ($p < 0.0001$). In contrast to the 200g load, there were significant differences ($p < 0.044$) in the specific wear rate of the unreinforced and the *H. sabdariffa* fibre-reinforced denture base acrylic resins at the 500g load. The hardness values revealed no significant differences ($p > 0.707$) between the two sample groups. There were however, significant differences ($p < 0.041$) in the water absorption rate between the two sample groups.

Overall, the prominent features of this study showed that *H. sabdariffa* fibre is a suitable reinforcement fibre material for denture base acrylic resins and is in compliance with ISO 1567: 1999. Although this study found that *H. sabdariffa* fibres can be used as reinforcement material for denture base acrylic resins, the results cannot be generalised to clinical conditions, therefore in vitro and in vivo investigations are recommended.

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Acromyms and Terminology

Within this dissertation various acronyms and terminologies as outlined below are used.

Acronyms

ANSI/ADA	American National Standard/American Dental Association
ASTM	American Society for Testing and Materials
DUT	Durban University of Technology
FAO	Food and Agricultural Organisation
FE-SEM	Field Emission Scanning Electron Microscope
FS	Flexural Strength
FT-IR	Fourier Transform Infrared Spectroscopy
H_2O	Water
H_2O_2	Hydrogen peroxide
IS	Impact Strength
ISO	International Standard Organisation
KJ/M^2	Kilojoule per Metre square
$KMNO_4$	Potassium Permanganate
KOH	Potassium Hydroxide
LiOH	Lithium Hydroxide
MA	Maleic Anhydride
MPa	Mega Pascal
MOE	Modulus of Elasticity
Na	Sodium
NaOH	Sodium Hydroxide
OH	Hydroxyl Group
O_2	Oxygen
PALF	Pineapple Leaf
PLA	Poly (lactic acid)
PP	Poly Propylene

RPM	Revolutions per Minute
ROOR	Peroxide Functional Group
SPSS	Statistical Package for Social Science
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis
UKZN	University of KwaZulu-Natal
Wt%	Weight Percentage

Terminology

1. Biocompatibility: The ability of a material to perform, as intended, with minimal biological response in harmony with the body environment (tissue) without causing negative, or having destructive effects on the biological functions of the body. This involves an interaction or influence between the biological environment and the material as the material can either influence or be influenced by the body. This influence, which can be local (site of contact) or systemic (away from site of contact), is dependent on the composition of material, length of stay in the body, the body concerned, and the condition of the body. In relation to a denture, it refers to the optimal performance of the denture without causing a negative or pathological response by the oral tissues (Weiss and Weiss 2001; von Noort 2008; Anusavice and Schmalz 2013).

2. Composite: A structural material made up of two or more distinct materials or phases with properties which are superior to those of the individual materials or phases, and which are insoluble in each other (Malhotra *et al*. 2012). The term specifically refers to structural materials (matrices) within which fibrous materials (reinforcements/fillers) are embedded. Composites are generally stiff and strong for their weight and are easily moulded into different shapes. These are characteristics that make composites useful in different applications where weight is a concern (Smith 1996; Dyer *et al*. 2004; von Noort 2008; McCabe and Walls 2009; Thiruchitrambalam *et al*. 2010).

3. Denture: A removable prosthodontic dental appliance designed and constructed which carries tooth/teeth on a base to replace lost or missing tooth/teeth and associated tissues of the oral cavity. Dentures are either complete or partial and are made up of different parts including base, teeth and sometimes flange and border (Veeraiyan, Ramalingam and Bhat 2009; Bonsor and Pearson 2013).

4. Denture base: That part of the denture which rests on the mucosa, replaces lost tissues, and carries the attached tooth/teeth. Denture bases are made either of metals or non-metals. Metals include gold alloys, chrome cobalt alloy or Ni-Cr alloys (Veeraiyan *et al*. 2009; Tandon, Gupta and Agarwal 2010). Non-metals include acrylic resins, vinyl resins, vulcanite, phenolic resins etc. (Manappallil 2004; von Noort 2008; Veeraiyan *et al*. 2009; Tandon *et al*. 2010).

5. Fibre pull-out: This is a phenomenon of separation of fibre from matrix due to insufficiency of adhesion between the two materials in a composite. This is responsible for premature fibre failure in a matrix environment. In such cases, the fibre does not contribute to the composite hence adversely impacting on the strength of the material (Dassios 2007).

6. Flexural strength (*FS*): The ability of a material to withstand repeated or continuous stress on it. In relation to acrylic resin denture, FS is the ability of the denture to withstand repeated low stress placed on it as a result of a series of mastication or biting forces (McCabe and Walls 2009; Bolos *et al*. 2013).

7. Glass transition temperature (*Tg*): The temperature at which polymeric (amorphous) materials change form from hard, glassy or brittle state to soft, rubbery or liquefied state. Glass transition temperature is an elevated temperature at which the amorphous polymer chains undergo increased mobility causing softening or phase change. In semi-crystalline materials, Tg is a temperature range well below the melting point, and marks the temperature at which, on cooling, the molecules start impeding each others' movement. Glass transition temperature is a reversible transition and is reported as the

midpoint of the temperature range. Polymethyl methacrylate (PMMA) is used below its Tg which is 100 ^oC (Rieger 2001; Liu *et al*. 2009b; and Calonego *et al*. 2010).

8. Impact strength (*IS*): The ability of a material to resist a sudden blow or rapid stress placed on it without deformation, crack or fracture. In relation to acrylic denture, IS is the ability of the denture to resist fracture due to impact in the mouth or accidental dropping outside the mouth (McNally *et al*. 2006; Faruk *et al*. 2012; Anasane *et al*. 2013).

9. Matrix: A primary structural material onto which secondary (reinforcing) material is added for the improvement of properties. Matrix binds the reinforcement together and gives body to the composite. They are often polymers, organic or inorganic materials (Taj *et al*. 2007).

10. Mercerisation: A chemical (alkali) treatment process applied to plant fibres to permanently impart a greater affinity for various finishes. The process has t following chemical equation:

    $$\text{Fibre} - OH + NaOH \rightarrow \text{Fibre} - O - Na + H_2O$$

    Mercerisation helps to improve arrangement, scope, character, surface roughness and reactive sites, and mechanical properties of fibres (Li *et al*. 2007; Modibbo *et al*. 2009; Kalia *et al*. 2009; Hashim *et al*. 2012).

11. Modulus of elasticity (*MOE*): The degree of stiffness of a material. Also referred to as Young's modulus, bulk modulus, modulus of rigidity or tensile modulus. It is the ratio of the stress applied to a body or substance to the resulting strain within elastic limit. It denotes the measure of an object's or a substance's resistance to elastic deformation when force is applied to it. In a graph depicting stress-strain curve, it is the slope of the linear segment before the plastic deformation of the material. The higher the MOE the stiffer the material and the less elastic strain caused by applied force (Dyer *et al*. 2005; Rodrigues-Junior *et al*. 2007).

12. Polymer: A chemical product of higher molecular-weight macromolecules formed as a result of chemical reactions between lower molecular-weight molecules known as monomers (Rawls 2013).

13. Prosthodontics: Branch of dentistry which deals with the replacement of form and functions of tissues (teeth, parts of alveolar ridge and mucous membrane) using removable appliances such as partial denture for dentate and complete denture for edentulous cases (Veeraiyan *et al*. 2009).

14. Reinforcement: The process of improving the properties of a primary material (matrix) by the intimate blending of one or more materials into it to form an integral body having properties different from and superior to the individual component materials (Franklin *et al.* 2005 and Alla *et al*. 2013).

15. Residual monomer: The unreacted free radical of the un-polymerised monomer in denture base acrylic resins. During the conversion of monomers to polymers (polymerisation) of acrylic resins, however, not all monomers are converted into polymers. These remain in the mass and are termed residual monomers. These residual monomers usually have consequences on the dentures as they act as plasticisers thereby adversely affecting the mechanical properties of dentures. Similarly, they leach out of the denture intra-orally and are considered responsible for a certain level of cytotoxicity of denture base acrylic resins (Koroglu *et al*. 2012; Ivkovic *et al.* 2013).

16. Retting: The process of breaking the bond between the bast fibres and the plant woody core, and converting the fibre bundles into individual fibres. The process involves using microbes or chemicals to degrade the pectin rich bast and lignin in the middle lamella which is connected to the adjacent fibre cells in order to release the individual fibres. There are about five types of retting processes, namely: dew/field retting; water retting; enzymatic retting; chemical retting; and mechanical retting (Biagiotti *et al*. 2004; Tahir *et al*. 2011).

Chapter 1 – Introduction

1.1 Background and Context of the Study

Several studies (Goguta *et al*. 2006; Vodjani and Khaledi 2006; Ayad, Badawi and Fatah 2008; Rahamneh 2009; Vojvodic *et al*. 2009; Gurbuz, Unalan and Dikbas 2010; Ferracane 2001; Vodjani, Bagheri and Khaledi 2012; Arafa 2012) have reported that denture base acrylic resins are commonly used in the fabrication of dentures because they closely approximate the colour of the oral cavity, are easy to repair, are non-toxic, and are light in weight. In spite of these characteristics, Tacir *et al*. (2006), Koroglu, Ozdemir and Usanmaz (2009), and Alla *et al*. (2013) claim that denture base acrylic resins have low impact strength (IS), poor fatigue resistance, low hardness and wears easily. Consequently, these make acrylic dentures susceptible to fracture on impact or through fatigue stress in the mouth. According to Bashi and AL-Nema (2009: 57) low fatigue resistance is the main reason for midline fractures of complete dentures. Hence, and as advised by several authors (Unalan, Dikbas and Gurbuz 2010; Vodjani, Bagheri and Khaledi 2012; Alla *et al*. 2013), metal powders such as silver, copper, aluminium particles, and synthetic fibres such as glass, aramid, and polyethylene fibres can be used to reinforce acrylic dentures, which in turn improves strength.

Apart from the high costs, Tacir *et al*. (2006), Vodjani and Khaledi (2006), and Geerts, Overturf and Oberholzer (2008) explained that while metal powders improve the strength of acrylic dentures, they are generally difficult to apply during fabrication and are prone to corrosion intra-orally. Furthermore, they indicated that metal powders are non-degradable, non-recyclable and are not environmentally friendly. More importantly, Mowade *et al*. (2012: 30) and Alla *et al*. (2013: 92) pointed out that there is a lack of interfacial bond between the metal and acrylic resins due to the increased stress concentrations around the embedded metal inserts. Tacir *et al*. (2006), Goguta *et al*. (2006), Vodjani, Bagheri and Khaledi (2012) and Alla *et al*. (2013) therefore advocate using natural fibres to reinforce dentures to facilitate improvement in the mechanical properties of polymers.

Essentially, and as pointed out by Anbukarasi and Kalaiselvam (2015: 321), natural fibres such as *Hibiscus sabdariffa*[1] are non-toxic to the body. *H. sabdariffa* fibre is obtained through retting of the plant bast, which is processed in terms of its use and application (Thakur *et al*. 2012). Singha and Thakur (2008a: 552) and Ahmad, Choi and Park (2015: 14) have further indicated that *H. sabdariffa* provides strong reinforcement when mixed with polymer matrices for automobile and orthopaedic accessories due to its high strength, toughness and stiffness, low density, and good tensile modulus. Although natural fibres have replaced synthetic fibres, there has been very limited research on the use of natural fibres to reinforce acrylic dentures. This study aimed to investigate the suitability of *H. sabdariffa* as fibre reinforcement material for denture base acrylic resins, particularly focussing on the flexural strength (FS) and impact strength (IS) of the composite.

1.2 Statement of the Problem

Goguta *et al*. (2006: 88) and Kiilu (2008: 2) indicated that patients incur additional costs of repairing dentures that break within a few years of intra-oral use. From a dental technology laboratory perspective, and as argued by Alla *et al*. (2013), while there are various reinforcing materials such as metal powders used to improve the low strength and poor fatigue resistance of acrylic dentures, these materials show poor interfacial bonding with the matrix. Equally important, and from a biological perspective, Kim and Watts (2004) and Vodjani and Khaledi (2006) asserted that metal inserts are prone to corrosion and are difficult to handle during fabrication. Synthetic fibres are therefore used as an alternative reinforcement material; however, some researchers have confirmed that they are non-biodegradable, not environmentally friendly (Thakur *et al*. 2012), have high water absorption and are toxic in nature (Ozen *et al.* 2006). Thus, reinforcement of acrylic resins with a material that does not pose a threat to patients or the environment and does not compromise the characteristics of the material is desirable.

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[1] **From this point forward, the botanical name *H. sabdariffa* will be used.**

1.3 Aim

To investigate the suitability of *H. sabdariffa* as a fibre-reinforcement material for denture base acrylic resins.

1.4 Objectives of the Preliminary and pilot Studies

To determine the characteristics of *H. sabdariffa* fibre as a reinforcing material by ascertaining:

1.4.1 The physical characteristics of *H. sabdariffa* fibres as a potential reinforcement material.

1.4.2 The weight percentage of *H. sabdariffa* fibres required to reinforce denture base acrylic resins.

1.4.3 The length of *H. sabdariffa* fibre required to reinforce denture base acrylic resins.

1.5 Objectives of the Main Study

To determine the suitability of *H. sabdariffa* fibre as a reinforcing material by examining the:

1.5.1 Flexural strength and impact strength of *H. sabdariffa* fibre-reinforced denture base acrylic resins at different conditioning temperatures in order to set parameters for comparison with the control.

1.5.2 Hardness, wear resistance, and water absorption behaviour of the reinforced denture base acrylic resins.

1.5.3 Microstructure of *H. sabdariffa* fibre-reinforced denture base acrylic resins in order to ascertain if it is a suitable reinforcement material. This was investigated in line with ISO 1567 (1999).

1.6 Rationale for the Study

While the literature documents the usefulness of *H. sabdariffa* as a reinforcement material (Fuqua, Huo and Ulven 2012; Chauhan and Kaith 2012; Taj, Munawar and Khan 2007; Singha and Thakur 2008a; Chandramohan and Marimuthu 2011), research has focused mainly on its use to reinforce industrial polymer matrices for shoes, toys, cars, and aeroplanes, among others. In light of *H. sabdariffa* being used for reinforcing industrial polymer matrices, it is envisaged that this fibre could also be used to reinforce acrylic dentures due to its high strength, toughness and stiffness, low density, and good tensile modulus and biocompatibility. This study therefore sought to use *H. sabdariffa*, which is widely available in Nigeria, as a fibre reinforcement material for acrylic dentures. Significantly, and as highlighted by Omobuwajo *et al*. (2000) and Padmaja *et al*. (2014), *H. sabdariffa* is fairly safe to use particularly in view of its use in the food and beverage industries.

1.7 Hypotheses

H_0: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres does not improve the flexural strength properties.
H_1: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres improves the flexural strength properties.

H_0: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres does not improve the impact strength properties.
H_1: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres improves the impact strength properties.

H_0: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres does not improve wear resistance and hardness properties.
H_1: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres improves wear resistance and hardness properties.

H_0: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres does not improve resistance to water absorption.

H_1: Reinforcement of denture base acrylic resins with *H. sabdariffa* fibres improves resistance to water absorption.

1.8 Assumptions

1.8.1 *H. sabdariffa* is widely used in the medical field, for example in the treatment of hypertension (Mckay *et al*. 2010), diabetes (Adeyemi *et al*. 2014; Andraini and Yolanda 2014), implants/orthopaedics (Chandramohan *et al*. 2010), wound healing (Builders *et al*. 2013), and cancer (Khaghani *et al*. 2011). Hence, it is assumed that it can be safely used as a fibre reinforcement material for denture base acrylic resins.

1.8.2 All data collection instruments were deemed valid and reliable based upon their use and calibration period in the University and other institutions.

1.8.3 The standards selected for property determination were applicable to, and suitable for, the type of materials being tested in this study.

1.9 Delimitations

1.9.1 Although there are many brands of acrylic denture base materials available on the market, this study only used Vertex™ (Vertex Dental BV, Zeist, The Netherlands) heat-cured acrylic resin because it is the material commonly used in South Africa. A noteworthy point is that this acrylic resin conforms to ISO 1567: 1999, which is the equivalent of ANSI/ADA specification No. 12: 2002 of denture base resins. Hence, Vertex™ rapid simplified heat-cured acrylic resin is deemed suitable for the study.

1.9.2 While there are several natural fibres available on the market, only *H. sabdariffa* fibre was considered in this study.

1.9.3 Although there are several chemicals used to treat natural fibres, the process of mercerisation was chosen as the method to treat the *H. sabdariffa* fibres. Mercerisation is an easy method, enables effective interfacial bond between fibres and polymer matrices, and has the least effect on the environment (Alam *et al*. 2015).

1.10 Limitations of the Study

1.10.1 Any conclusions drawn from the results of this study relate solely to the materials used and prepared under a similar methodology. Hence, the results cannot be generalised to all denture base acrylic resins/natural fibres composites that are prepared using different methodologies.

1.10.2 While the results of this study may have application, it cannot be generalised to clinical conditions.

1.11 Structure of the Dissertation

The dissertation is divided into five chapters as follows:

Chapter 1 presents the context of the study by detailing the positive qualities of acrylic resins, which made it a popular choice of material in the fabrication of dentures. The poor mechanical properties associated with the material, which makes it prone to fracture on impact or through fatigue stress have also been highlighted. Subsequently, the chapter explained the various efforts aimed at improving the mechanical properties which included but were not limited to reinforcement using metals and synthetic fibres. The deficiencies of these materials which made them inappropriate as reinforcement was further highlighted. In view of the deficiencies of the various reinforcements, the need for an alternate material such as *H. sabdariffa* fibres has been identified. This led to the statement of the problem, aim and objectives, the rationale for the study, hypothesis, assumptions, delimitations and scope of the study.

Chapter 2 provides an overview of the literature related to denture base materials. This includes a historical review of denture base materials, together with an explanation on the ideal properties of denture base materials. This leads to a discussion on the challenges experienced in reducing the problems related to reinforcing acrylic dentures. Subsequently, *H. sabdariffa* fibres as a reinforcing material, the process of retting and chemical treatments are discussed.

Chapter 3 describes the research design and methodology by detailing the quantitative research paradigm and experimental research methods adopted in the preliminary, pilot and main studies.

Chapter 4 presents the statistical results and discusses the reinforcing characteristics of *H. sabdariffa*. Tables, graphs, charts and images are used to support the analytical results.

Chapter 5 presents the conclusions drawn from the study and identifies limitation(s) while offering future directions for research.

Chapter 2 – Literature Review

2.1 Introduction

This chapter reviews literature related to the mechanical properties of denture base acrylic resins with an emphasis on their FS and IS. Initially, this chapter provides an overview of the ideal requirements of denture base materials. This understanding is pertinent to the historical development of the various denture bases materials. Subsequently, the properties of denture base acrylic resins, with an emphasis on the properties that causes denture base acrylic resins to fracture intra-orally and extra-orally, are discussed. The attempts made to improve the mechanical properties of the material are described. The review then focuses on fibres used to reinforce denture acrylic resins, with an emphasis on *H*. *sabdariffa* as a potential fibre reinforcement material for denture base acrylic resins. This is followed by a discussion on fibre retting and fibre modification methods used to improve the interfacial bond between fibres and polymer matrices. Finally, the chapter concludes by summarising the contents of the literature review undertaken.

As documented in the literature (Combe 1992; Craig 1993; McGivney and Carr 2000; von Noort 2008; McCabe and Walls 2009; Bonsor and Pearson 2013) there are five broad categories of ideal requirements for denture base materials. Table 2-1 presents a detailed description of each category, namely: Physical, Chemical, Biological, Mechanical, and Sundry. This is the point of departure for the next section.

2.2 Historical Overview of Denture Base Materials: In Brief

Dentures are generally fabricated to replace missing teeth and the surrounding soft tissues. McGivney and Carr (2000), Jepson (2004), Veeraiyan *et al*. (2009), Johnson and Wood (2012) and Johnson *et al*. (2016) described the denture base as that part of the denture that rests on the mucosa, replaces lost alveolar tissues and holds the artificial teeth. As presented in Table 2-2, prior to the introduction of denture base acrylic resins, several other materials such as gold plates mounted on gold springs and swivels, vulcanite, cellulose products, phenol formaldehyde, vinyl plastics and other synthetic resins were used as denture base materials (Rueggerberg 2002; Manappallil 2004; von Noort 2008; McCabe and Walls 2009; Tandon *et al*. 2010; Rawls 2013). These materials were however, difficult to handle and adjust, dimensionally unstable, produced odour and allergy intra-orally, and consequently considered clinically unacceptable. In view of the limitations of the above denture base materials, and the pursuit of clinically and aesthetically acceptable denture base materials, denture base acrylic resins were introduced. The next section reviews the qualities of denture base acrylic resins, especially in relation to the ideal requirements.

2.3 Denture Base Acrylic Resins

According to Vojvodic *et al*. (2008: 1023) acrylic resins, which were introduced in 1937, gained widespread acceptance as denture base material as they fulfilled most of the criteria of the ideal requirements as presented in Table 2-1. Unfortunately, and as asserted by several authors (Franklin *et al*. 2005; Tacir *et al*. 2006; Koroglu *et al*. 2009; Gurbuz *et al*. 2012; Alla *et al*. 2013; Mahajan *et al*. 2014; Hamouda and Beyari 2014), denture base acrylic resins have weak mechanical properties, particularly low IS and poor FS. Consequently, acrylic dentures are prone to fracture on impact, or through fatigue stress in the mouth. McNally *et al*. (2006), Anasane *et al*. (2013) and Bolos *et al*. (2013) defined FS as the ability of acrylic resin to withstand repeated low stresses during intra-oral function such as the forces of mastication. Significantly, and as explained by Gurbuz *et al*. (2012), the ability of a denture to resist these stresses is an important mechanical property in determining the durability of the appliance in use. Goguta *et al*. (2006) and Dikbas *et al*. (2012) elaborated that IS, by contrast, is the ability of acrylic resins to resist rapid stresses such as sudden strike or accidental dropping of the dental appliance outside the mouth during cleaning, strong coughing, or sneezing.

Table 2-1: Ideal requirements of denture base material

Categories	Details	References
1. Physical	1.1 Colour to simulate the natural oral tissues and to be stable in the mouth; 1.2 Ability to be tinted or pigmented; 1.3 Has glass transition temperature to prevent softening and distortion during use; 1.4 Must be dimensionally and thermally stable; 1.5 Have a high diffusion co-efficiency; 1.6 Low specific gravity; 1.7 Absence of taste and odour; 1.8 Radiopaque; 1.9 Accurate reproduction of surface details; 1.10 Good fit and comfort to oral tissues; 1.11 Permit food taste; and 1.12 Thermal expansion matching to artificial tooth material.	Combe 1992; Craig 1993; McGivney and Carr 2000; von Noort 2008; McCabe and Walls 2009; Bornsor and Pearson 2013
2. Chemical	2.1 Must be chemically inert; 2.2 Insoluble in, and impermeable to, oral fluids and water; 2.3 Chemically stable in all forms (powder, liquid, block); and 2.4 Ability to chemically adhere to plastics, metals porcelain and other denture components.	
3. Biological	3.1 Biocompatible (non-toxic and non-irritant to the oral tissues); and 3.2 Should not promote bacterial/fungal growth.	
4. Mechanical	4.1 Adequate strength (flexural and impact); 4.2 Stiffness and resilience; 4.3 High proportional limit; 4.4 Good hardness and toughness; 4.5 Wear and abrasion resistance; and 4.6 Retains high polish.	
5. Sundry	5.1 Easily manipulated and repaired; 5.2 Ease of cleaning; 5.3 Inexpensive; 5.4 Good shelf life; and 5.5 Non-traumatisation of oral tissues.	

Source: Adapted by the researcher

Table 2-2: Summary of denture base materials from early development to the introduction of acrylic resins

Materials *(Year)*	**Strengths**	**Weaknesses**	**References**
Wood, bone and ivory *(Prior to 1778)*	Readily available; Cheap; Easy to manipulate.	Unhygienic; Unaesthetic.	Khindra *et al*. 2009; Tandon *et al*. 2010.
Porcelain *(1778)*	Easy to manipulate; Simulates colour of the soft tissues; Adapts well to the underlying tissue; Low water absorption and stability; Minimal porosity.	Fractures easily; Difficult to grind and polish.	Manappallil 2004; Khindria *et al*. 2009; Tandon *et al*. 2010.
Vulcanite *(1859)*	Easy to manipulate and repair; Adapts well to the underlying tissue thereby increases patient comfort; Cheap; Durable; Light weight; Non-reactive and insoluble in oral fluids.	Poor aesthetics (dark brown/red colour); Absorbs saliva hence dimensionally unstable; Unhygienic and produces an odour.	Johnson 1959; Combe 1986; Rueggerberg 2002; Manappallil 2004; Gelbier 2005; von Noort 2008; Khindria *et al*. 2009; Tandon *et al*. 2010; Ladha and Verma 2011.
Aluminium *(1867)*	Good fit and strength (in thin section); Good thermal conductivity; Light weight.	Expensive; Difficult to handle and repair; Has been linked to Alzheimer's disease.	Khindria *et al*. 2009; Ladha and Verma 2011.
Celluloid *(1869-1870)*	Initially excellent aesthetics (pink and translucent); Easy to manipulate; Economical; Elastic thereby easily adapts to retentive structures.	Discoloured over time; Gradual dissolution in oral fluids; Leached camphor and produces odour; Poor thermal conductivity; Required specialised expertise.	Rueggerberg 2002; Manappallil 2004; Gelbier 2005; von Noort; Khindria *et al*. 2009; Tandon *et al*. 2010; Ladha and Verma 2011.
Stainless steel, silver and base metal alloys *(1907)*	Light weight; Low cost; High resistance to tarnish and corrosion; Good strength in thin sections.	Difficult to manipulate and adjust; Allergic reaction in the mouth.	Khindria *et al*. 2009; Tandon *et al*. 2010.
Phenol formaldehyde *(1909)*	Good aesthetics; Readily available.	Difficult to handle and repair; Brittle and fractured easily; Lacked uniformity.	Combe (1986); Manappallil 2004; von Noort 2008; Khindria *et al*. 2009; Tandon *et al*. 2010; Rawls 2013.
Vinyl polymers *(1912)*	Good aesthetics.	Difficult to manipulate; Warped in the oral cavity; Poor fracture resistance.	Combe 1986; Rueggerberg 2002; von Noort 2008; Khindria *et al*. 2009; Tandon *et al*. 2010; Rawls 2013.

Source: Adapted by the researcher

From a clinical perspective, Goguta *et al*. (2006) and Kiilu (2008) asserted that denture acrylic resins fracture within a few years of clinical service. Consequently, patients incur additional costs of repairing their dentures. Importantly, Franklin *et al*. (2005) argued that the fracture of denture base acrylic resins is a health risk if patients accidentally inhale or swallow it as it not radiopaque. According to several scholars (McCabe and Walls 2009; Ihab and Moudhaffar 2011; Bonsor and Pearson 2013), denture base acrylic resins are radiolucent and cannot be detected by x-ray. El-Shereksi *et al*. (2009), Tandon *et al*. (2010) and Nandal *et al*. (2013) however, reported that adding materials such as barium titanate, 10-15% bismuth, uranyl salts or 35% organo-zirconium material or triphenyl bismuth (Ph_3Bi) could make acrylic resins radiopaque. These materials however, trigger cytotoxicity, increase water absorption and transverse deflection, which, in turn, reduce the mechanical properties of acrylic dentures.

As several studies (Vodjani and Khaledi 2006; Lee *et al*. 2007; Unalan *et al*. 2010; Vodjani *et al*. 2012; Morsy and Al-Daous 2013) have indicated, that denture fracture can be reduced by reinforcing acrylic resins during fabrication procedures. Ultimately, this will help improve the mechanical properties. The following section will review the various efforts at improving the mechanical properties of denture base acrylic resins, particularly the FS and IS.

Table 2-3: Summary of poor qualities/properties of denture base acrylic resins in relation to the ideal requirements of denture base materials

Ideal requirements of denture base materials	Poor qualities/properties of acrylic resins	References
Physical requirements		Combe 1992; McGivney and Carr 2000; Azzarri *et al*. 2003; Manappallil 2004; Lung and Darvell 2005; Meng and Latta 2005; El-Sheikh and Al-Zahrani 2006; Ayad *et al*. 2008; Karaagaclioglu *et al*. 2008; von Noort 2008; McCabe and Walls 2009; Kostic *et al*. 2009 Rahamneh 2009; Gurbuz *et al*. 2010; Ihab and Moudhaffar 2011; Bonsor and Pearson 2013; Powers and Wataha 2013; Soygun, Bolayir and Boztug 2013; Jaikumar *et al*. 2014; Reddy *et al*. 2014; and Thomas *et al*. 2015.
▪ Aesthetics and permanence of colour; ▪ High softening temperature; ▪ Dimensional stability; ▪ Good thermal conductivity/diffusion; ▪ Low specific gravity; ▪ Absence of odour and taste; ▪ Radiopacity; ▪ Good reproduction of surface details and high polish; ▪ Permit food taste; and ▪ Comfort to patient.	▪ Non-radiopaque (radiolucent); and ▪ Poor thermal conductivity.	
Chemical requirements		Craig 1993; von Noort 2008; McCabe and Walls 2009; Palitsch *et al*. 2012; Bonsor and Pearson 2013; Mathew Shenoy and Ravishankar 2013; Rawls 2013.
▪ Chemical inertness; ▪ Insoluble and non-absorbance of oral fluids; ▪ Chemical stability in storage; ▪ Adherence to teeth and other material components of denture.	▪ Absorbs water (2% expansion).	
Mechanical requirements		Tacir *et al*. 2006; Vodjani and Khaledi 2006; Lee *et al*. 2007; Kiilu 2008; Koroglu *et al*. 2009; Unalan *et al*. 2010; Dikbas *et al*. 2012; Vodjani *et al*. 2012; Alla *et al*. 2013; Morsy and Al-Daous 2013; Powers and Wataha 2013; Hamouda and Beyari 2014; Mahajan *et al*. 2014; Thomas *et al*. 2015.
▪ Adequate strength, stiffness and resilience; ▪ Hardness and abrasion resistance; and ▪ High proportional limit.	▪ Low/poor strength; ▪ Low modulus of elasticity, and ▪ Poor abrasion resistance.	

Source: Adapted by the researcher

2.4 An Overview of the Efforts Towards Improving the Mechanical Properties of Denture Base Acrylic Resins

According to Franklin *et al*. (2005: 366) and Alla *et al*. (2013: 91), FS and IS of dentures can be improved through chemical modification of acrylic resins. This involves the use of cross-linking agents and graft co-polymers to develop new materials such as poly carbonates and polyamides. Significantly, Machado *et al*. (2007) noted that none of the developed materials has proved to be superior to denture base acrylic resins. In comparison with acrylic resins, von Noort (2008) indicated that the new materials were costly, absorb excess water and were highly flexible due to low elastic modulus. Reinforcements such as metals and synthetic fibres were therefore used to improve the strength of acrylic dentures. For example, Karacaer *et al*. (2003) concluded that using 4mm, 6mm, and 8mm glass fibres at different concentrations (1%, 3%, and 5%) significantly improved the overall strength of acrylic resins. Similarly, Bashi and Al-Nema (2009) found that the transverse and IS improved when glass fibres were differently orientated (woven, random and aligned) in the acrylics resins. The work of the aforementioned authors are further supported by several other scholars (Dogan *et al*. 2008; Geerts *et al.* 2008; Iqbal and Naqash 2014; Thomas *et al*. 2015) who demonstrated that glass fibre reinforcements improve the mechanical properties of denture base acrylic resins.

Recently, Murthy *et al*. (2015) confirmed that polyethylene fibre significantly improved the IS of denture base acrylic resins by 158%. In contrast, Uzun *et al*. (1999), Geerts *et al*. (2008), Kamble, Parkhedkar and Mowade (2012), and Ismaeel, Alalwan and Mustafa (2015) showed that there were no significant improvements in the fracture toughness, FS and IS of denture base acrylic resins reinforced with polyethylene fibres. They attributed the weak results to the poor interfacial union between the acrylic resins and the fibres. Similarly, Dogan *et al*. (2008) demonstrated that nylon, rayon, glass and polyester fibres did not improve the FS of denture base acrylic resins.

Several other authors (Kim and Watts 2004; Vodjani and Khaledi 2006; Hirajama, Takahashi and Minakuchi 2009; Jaber 2011) articulated the inherent disadvantages of using metals such as that metals are difficult to handle during processing procedures, are expensive, and corrode easily in the mouth. Geerts *et al*. (2008) also noted that while some synthetic fibres provide better reinforcement to denture base acrylic resins, they are expensive and difficult to manipulate during processing. Ayad, Badawi and Fatah (2008) and Farina *et al*. (2012) claimed that the mechanical properties, hardness and wear resistance, and service life of materials are closely and proportionally related. As hardness and wear resistance are supporting concepts in this study they are discussed in the next section.

2.4.1 Hardness and Wear Resistance

Mathew, Shenoy and Ravishankar (2014: 71) asserted that hardness and wear resistance are interrelated mechanisms that determine the mechanical behaviour and service life of materials including dentures in service. Arora, Singh and Arora (2015) further elaborated that hardness of a denture indicates the ease with which the denture is finished and its resistance to scratching while in use. According to Ahmed and Ebrahim (2014: 54) and Hamanaka *et al*. (2016: 32), hardness is an important factor when evaluating the mechanical properties and predicting the wear resistance of dentures. From a clinical perspective, Gazal *et al*. (2008) and Arora *et al*. (2015) explained that oral restorative materials should be resistant to wear, have minimal or no abrasive effects, and help keep the oral tissues they are in contact with intact. Consequently, the clinical success of dentures is partially linked to the hardness and wear resistance of dentures as surface roughness attracts the adhesion of microorganisms, which could promote denture induced stomatitis and other diseases.

In evaluating the Vickers hardness of denture base acrylic resins reinforced with glass fibre, Farina *et al*. 2012 asserted that glass fibre reinforcement improved the hardness of various brands of acrylic resin by between 1% to 6%. Similarly, and in evaluating the effect of zirconia oxide nano-fillers on the hardness of acrylic resins, Ahmed and Ebrahim (2014) reported that the hardness of the composite material increased with an increase in zirconia oxide. They attributed this increase to the relative interfacial bond between the nano-fillers and the resin matrix. Mathew, Shenoy and Ravishankar 2014 found that reinforced denture base acrylic resins with polypropylene fibres of different weight percentages increased the hardness and wear resistance of the composite. Conversely, and as reported by Ayad, Badawi and Fatah (2008) and Asopa *et al*. (2015), denture base acrylic resins reinforced with zirconia showed no significant increase in hardness in comparison with conventional denture base acrylic resins. Similarly, authors (Azzarri *et al*. 2003; Lung and Darvell 2005; Kostic *et al*. 2009) highlighted that residual monomer in denture base acrylic resins contribute to poor mechanical properties and invariably reduce hardness. They argued that prolonged polymerisation and increased temperature reduce residual monomer hence improving the mechanical properties of denture base acrylic resins. Hardness and wear resistance of reinforced denture acrylic resins are pertinent to this study, and are included in the next chapter in terms of using the Barcol hardness test and the pin-on-disc wear test, respectively.

As posited by several authors (Wambua *et al*. 2003; Bax and Mussig 2008; Thiruchitrambalam *et al*. 2010; La Mantia and Morreale 2011; Kabir *et al*. 2012; Tewari *et al*. 2012), the associated high costs, limited availability, and cytotoxic effects, have adversely impacted on the use of synthetic fibres in denture reinforcements. Natural fibres are therefore being used as alternative materials to reinforce denture base acrylic resins, and is the point of the departure for the next section.

2.5 Natural Fibres

Natural fibres are elongated pieces of material that hold tissues together, which are processed into filaments, threads or ropes, and can subsequently be utilised as components of composite materials. According to Jacob *et al*. (2005: 95), there are three categories of natural fibres namely, mineral, animal and plant. They explained that plant fibres are lignocellulosic that is the major constituent is cellulosic fibrils that are held together by lignin and a hemicellulose matrix. Furthermore, and as elaborated upon by Kabir *et al*. (2012) and Fuqua, Huo and Ulven (2012), lignocelluloses also contain minor constituents such as pectin, wax, protein, tannins, ash and inorganic salts. Taj *et al*. (2007) and Singha and Thakur (2008a) argued that natural fibres provide superior reinforcement characteristics when applied to polymers. They asserted that they are non-toxic, renewable, biodegradable, environmentally friendly, and economical.

Plant fibres that are commonly used in the polymer composite industry include: henequen (Lee, Cho and Han 2008), areca (Mohankumar 2008), flax (Kaith *et al*. 2008; Raj *et al*. 2011), pine needle (Thakur and Singha 2011), banana (Ibrahim *et al*. 2010), sisal (Chandramohan and Marimuthu 2011), bagasse (Rodrigues *et al*. 2011), raphia palm (Obasi 2013), jute (Abdellaoui *et al*. 2015), and *H. sabdariffa* (Singha and Thakur 2009b; Chauhan and Kaith 2012; Chauhan 2013). Taj *et al*. (2007: 133) further pointed out that natural fibres when modified are used in the production of car seats, door panels, boats, and bullet proof vests. Table 2-4 presents the physical properties of some natural fibres.

Despite the benefits of cellulosic fibres in the reinforcement of composites, Chauhan and Kaith (2011) and Bhowmick, Mukhopadhyay and Alagisuramy (2012) have identified weaknesses such as poor wettability and high moisture absorption when mixed with polymer matrices. Consequently, there is a poor interfacial bond between the fibres and the polymer matrices. Other authors (Modibbo *et al*. 2009; Susheel, Kaith and Kaur 2009; Singha *et al*. 2009; Thakur *et al*. 2010; Chandramohan and Marimuthu 2010; Chauhan and Kaith 2012) therefore advocated using chemical modifications such as mercerisation, acetylation, etherification, silane coupling and graft copolymerisation to improve the interfacial lock between the fibres and the matrices. This, in turn, enhances the reinforcement characteristics of natural fibres. The aforementioned chemical treatments were taken into consideration when modifying *H. sabdariffa* fibres in this study.

2.6 *Hibiscus sabdariffa*

H. sabdariffa is a shrub of the Malvaceae plant family, which grows to approximately 3.5 metres. Several scholars (Mahadevan, Kamboj and Kamboj 2009; McKay *et al*. 2010; Khaghani *et al*. 2011; Padmaja *et al*. 2014; Adeyemi *et al*. 2014) reported that *H. sabdariffa* is cultivated mainly for the production of its leaves, flowers, seeds and calyces, which are used for beverages, tea, healthy drinks and for medicinal purposes. Chandramohan and Bharanichandar (2013) and Mwasiagi *et al*. (2014) argued that the bast fibres of *H. sabdariffa* are primarily sought as an alternative to synthetic fibres in the reinforcement of polymers and other industrial applications.

Additionally, and as asserted by others (Singha and Thakur 2008a; Chauhan 2013; Chauhan and Kaith 2013; Wen 2015), *H. sabdariffa* fibre is commonly used to reinforce polymers as they provide excellent reinforcement. Their argument is supported by Thiruchitrambalam *et al*. (2010) and Thakur *et al*. (2012), who used *H. sabdariffa* fibres to reinforce polyester and resorcinol formaldehyde matrices. While the aforementioned authors have indicated the diverse use of *H. sabdariffa* fibres, there is limited evidence on its use as reinforcing material for acrylic dentures.

Table 2-4: Physical properties of some natural fibres

Fibre Type	Density (g/cm^3)	Diameter (µm)	Water Content (%)	References
Jute	1.23 - 1.5	5 - 200	12.5 -13.7	FAO Corporate Document Repository 2003; Padmanabhan (n d); Taj *et al*. 2007; Modibbo *et al*. 2009; Summerscales *et al*. 2010; Kabir *et al*. 2011; Deepa *et al*. 2011; Jawaid and Abdul Khalil 2011; Jayabal *et al*. 2012; Fuqua *et al*. 2012; Sumaila *et al*. 2013; Senthiil and Sirsshti 2014; Shehu *et al*. 2014; Gurunathan, Mohanty and Nayak 2015; Pereira *et al*. 2015; Ramamoorthy, Skrifvars and Persson 2015; Pai and Jagtap 2015
Flax	1.4 - 1.5	5 - 38	10	
Ramie	1.5	18 - 80	7.5 - 17	
Kenaf	1.2 - 1.5	12 - 140		
Abaca	1.5	14 - 33	15	
Coir	1.2 - 1.5	40 - 450	8	
Hemp	1.14 - 1.5	10 - 53.7	6.2 - 12	
Pineapple	0.8 - 1.6	20 - 80	11.8	
Banana	1.3 - 1.5	13.16 - 280	10 - 12	
Sisal	1.2 - 1.5	7 - 200	10 - 22	
Cotton	1.21 - 1.6	12 - 35	7.8 - 8.5	
Luffa cylindrica	0.82	20 - 50		
Bagasse	0.55 - 1.25	10 - 34		
Bamboo	0.6 - 1.1	14 - 125	8.9	
Hard wood	0.3 - 0.88	16		
Soft wood	0.3 - 0.59	30		

2.7 Physical Characteristics of *H. sabdariffa* Fibre as a Reinforcing Material

Several scholars (Georgopoulos *et al*. 2005; Fuqua *et al*. 2012; Ahmad, Choi and Park 2015; Das and Biswas 2016) stated that lignocellulosic fibres are commonly used in the reinforcement of polymeric materials. They noted that the ability of the fibres to impart reinforcing effects on polymers is primarily caused by the cellulose content of the materials. Razali *et al*. (2015: 1808) showed that cellulose is the key component of fibres used in the reinforcement of composites which determine their mechanical performance. Furthermore, and as explained by Fuqua *et al*. (2012), cellulose contains an abundance of hydroxyl groups (OH), which lead to numerous hydrogen bonds with the hydroxyl groups of polymeric matrices. Consequently, and as asserted by Chauhan and Singh (2012), *H. sabdariffa* fibre as a lignocellulosic with high cellulose content enables it to reinforce polymeric materials, especially resorcinol formaldehyde. Resonating with the scholars above, Ghalehno and Nazerian (2011), and Ramu and Sakthivel (2013) further demonstrated that *H. sabdariffa* fibre is a good reinforcement material for polymers. They reinforced urea-formaldehyde particle board which resulted in higher bending strength.

Recently, Mwasiagi *et al*. (2014) and Nadlene *et al*. (2015) reported that the physical properties of *H. sabdariffa* fibre are integral to the mechanical properties of composites. These properties include, and are not limited to fibre diameter, fibre density, and moisture content and absorption behaviour of the fibre, all of which are reviewed in the subsequent sections.

2.7.1 Fibre Diameter

Fibre diameter is the dimension between the exterior surfaces and directly affects the aspect ratio (length/diameter). Arsene *et al*. (2013) and Pereira *et al*. (2015) maintain that the aspect ratio is critical in evaluating the efficiency of fibre as reinforcement in composites. This is consistent with Ashori (2008), Ashori and Nourbakhsh (2010) and Kabir *et al*. (2011) who state that a high-aspect ratio leads to improved mechanical properties of composites. Other scholars (Tomczak, Sydenstricker and Satyanarayana 2007; Hu *et al*. 2010; Fuqua *et al*. 2012; Everitt, Aboulkhair and Clifford

2013; Celino *et al*. 2014; Zannen *et al*. 2014; Shouha, Swain and Ellakwa 2014; Vallittu 2015) elaborated that an increase in the diameter of fibres decreases the aspect ratio and invariably the density. This adversely impacts the mechanical properties of fibres and composites, and vice versa. As seen from Table 2-4, variation exists in the diameters of different lignocellulosic fibres, hence ranges. The variation of diameters is generally due to inconsistency in the size of bundles of fibres. As highlighted by Bismarck, Misra and Lampke (2005), technically a single fibre consists of bundles of fibres, and it is difficult to measure individual fibres with the bare eyes. As noted by Chandramohan and Marimuthu (2011) the difficulty of obtaining individual fibres results in inconsistency in the physical properties of lignocellulosic fibres. Similarly, it can be observed that obtaining a particular diameter for *H. sabdariffa* fibres is difficult as each fibre sample presents different measurements at different spots within each fibre length.

As highlighted by Thakur, Singha and Thakur (2012) and Everitt, Aboulkhair and Clifford (2013), variation in physical properties of lignocellulosic fibres are due to location, source of plant, age, part of the plant, environmental condition, extraction technique, fibre microstructure, testing and characterisation techniques. According to De Rosa *et al*. (2010: 17), these factors are considered responsible for the variation and non-uniformity of diameters of natural fibres. Fibre diameter is important as aspect ratio of fibre (length/diameter) is a critical factor in reinforcement of polymers. As noted by Lee *et al.* (2008) and Shouha, Swain and Ellakwa (2014), very low aspect ratio weakens composites while mid and high-aspect ratio improves the mechanical properties of composites. This was taken into consideration as the diameter of *H. sabdariffa* fibre directly influences the mechanical properties of reinforced acrylic resins.

2.7.2 Fibre Density

The density of a material is directly proportional to its weight. Pradeep and Edwin (2015) emphasised that low density of fibres is a prerequisite to the reinforcement of composites. Their work supported Kabir *et al*. (2011) and Chandramohan and Bharanichandar (2013) who found that the light weight of natural fibres makes such fibres suitable reinforcement materials. Significantly, Razali *et al*. (2015: 1811) revealed that the presence of a lumen, a hollow channel within fibres, contributes to the low density of *H. sabdariffa* thereby making it a suitable polymer reinforcement material. Similarly, Goda and Cao (2007) had earlier asserted that low densities of natural fibre may be due to the presence of a lumen (hollow structure) in the fibre which is responsible for the lightweight of lignocellulosic fibres. The lightweight of the *H. sabdariffa* fibre is a necessary factor and advantage in composite materials. In addition, Zannen *et al*. (2014) showed that chemically treating lignocellulosic fibres affect the diameter and increase the density. They attributed this to the elimination of hollow structures from the fibres which exposes more cellulose for interaction with polymer matrix. This was considered in this study, as the density of *H. sabdariffa* fibre directly affects the properties of acrylic composite.

2.7.3 Moisture Content and Absorption

According to De Rosa *et al*. (2010: 117), Faruk *et al*. (2012: 1559 & 1560), and Zhu *et al.* (2013), lignocellulosic fibres contain water molecules within their structures. The moisture content is dependent on the non-crystalline component and the void contents of the fibres. Akil *et al*. (2011) pointed out that some lignocellulosic fibres contain as much as 20 % of water in their structures. Nadlene *et al*. (2015) and Razali *et al*. (2015) therefore advised that moisture content be considered in selecting lignocellulosic fibres for reinforcement of polymers. Celino *et al*. (2014: 2) cautioned that a higher moisture content of fibres will have a higher moisture absorption rate, which will negatively impact on the mechanical properties of the fibres and composites. Hence, and as reported by Razali *et al*. (2015), low water content fibres will effectively improve the life span of composites. They revealed that this may be due to the ability of the fibres to hold water which is then capable of degrading the composites.

Modibbo *et al*. (2007: 163) defined water/moisture absorbency as the percentage of water which dry fibres can absorb from the air under standard temperature and pressure at 25 ^{o}C and 65 % relative humidity. Concerningly, and as claimed by Alomayri *et al*. (2014), Celino *et al*. (2014), and Fiore, Di Bella and Valenza (2015), natural fibres have a high moisture absorption rate which therefore negatively affects the mechanical properties of composite materials. This aligns with the works of Akil *et al*. (2011) and Pandian *et al*. (2014), who revealed that water absorption leads to plasticisation and a weak interfacial bond between the matrices and fibres within composites. Consequently, the mechanical properties of composites are further reduced.

As asserted by Reddy and Yang 2005, Jawaid and Abdul Khalil 2011, and Faruk *et al*. 2012, moisture content and moisture absorption are closely related and affect the mechanical properties of composites. Martin *et al*. (2013) stated that the rate of moisture absorption and mechanical properties of composites are dependent on the moisture content of the fibres. According to Jawaid and Abdul Khalil (2011), fibres with a low moisture content are more likely to perform better with more service life in reinforcements than fibres with high water content. Additionally, the quantity of water absorbed by natural fibres and composites is dependent on factors such as composition, dimensions, surface protection, surface area, hydrophilicity and exposed time of the fibres, void fraction, and processing temperature of the composites. Equally significant, Razali *et al*. (2015) indicated that the high rate of lumen in fibres increases the rate of water absorption by the fibres and composites. Thiruchitrambalam *et al*. (2010), Mohan and Kanny (2011), and Das and Biswas (2016) concluded that there is a direct correlation between water absorption/content of fibres and the mechanical properties of the composites they reinforce. Essentially, they clarified that an increase in fibre content increases water absorption capacity of composites thereby decreasing their mechanical properties.

From a denture base acrylic resins perspective, Meloto *et al*. 2006 noted that water absorption within the ISO: 1567 limit (32 µg/mm^3) is necessary to compensate for polymerisation shrinkage. This effectively facilitates denture adaptation in the oral cavity. They elaborated that the higher the rate of polymerisation, the higher the water absorption rate in acrylic resins. Arora *et al*. (2015) further revealed that water absorption in denture acrylic resins produce approximately 0.23% linear expansion with an estimate of about 1% increase in weight over a period of time. Elias de Oliveira, Nogueira and Mattos (2014) and Hemmati, Vafaee and Allahbakhshi (2015) further clarified that the micro voids, or porosity, which occur among polymer chains during polymerisation promote water absorption thereby adversely affecting the mechanical, dimensional and colour properties of acrylic resins. In view of the arguments presented by the aforementioned authors, the water absorption behaviour of *H. sabdariffa* fibres and acrylic resins was considered in the research design of this study.

Moreover, and given the variability in the properties of lignocellulosic fibres, several authors (Puglia, Biagiotti and Kenny 2005; Thiruchitrambalam *et al*. 2010; Akil *et al*. 2011; Faruk *et al*. 2012) asserted that such fibres are unlikely to be uniform. Hence, prediction of the properties of their composites is difficult. In an attempt to reduce variability, several scholars (Li *et al*. 2007; Thomas and Pothan 2008; Kalia *et al* 2009; Rokbi *et al*. 2011; Fuqua *et al*. 2012; Panyasart *et al*. 2014; Saha *et al*. 2015) therefore advocated modifying fibre surfaces to promote effective bond with polymer matrices. This is discussed later in the chapter.

2.8 Effect of Fibre Content in Reinforcement of Polymers

Fuqua *et al*. (2012: 300) argued that very high percentages of fibres weaken composites. They therefore recommended using between 20% to 50% fibre content to reinforce polymer materials. Equally important, and according to Singha and Thakur (2008a: 552), the mechanical properties of composites increased when fibre content and weight percentage (wt%) increased by 30%. Subsequently, Thakur and Singha (2011) confirmed that 30 % volume of pine needle fibres in the reinforcement of phenol formaldehyde provided optimum mechanical properties. Furthermore, they elaborated that the mechanical properties (strength) decreased when the fibre content increased beyond 30%. They reported that with a high volume of fibre, the fibre-to-fibre contact in the composite increases and this breaks the ability of the matrix to transfer stress to the reinforcing material. A more recent study by Thakur, Singha and Thakur (2013) showed that 30% content of *H. sabdariffa* fibre recorded the highest mechanical properties in the reinforcement of urea-formaldehyde matrix. Similarly, Chauhan and Kaith (2013) outlined that optimum mechanical properties are achieved in the reinforcement of phenol formaldehyde when approximately 26.19% of *H. sabdariffa* is added. They agreed that either insufficiency or excess quantity of fibre leads to decreased strength of the composite.

Athijayamani *et al*. (2008) showed that the fibre content of a hybrid of *H. sabdariffa* and sisal in a polyester based composite positively affected the mechanical properties of the material. They clarified that increasing the fibre content to 45 wt% caused the tensile and FS of the composite to increase and the IS to decrease. Athijayamani *et al*. (2008) confirmed that increasing the quantity of fibres beyond 45 wt% had little effect on the mechanical properties of the composite. They further revealed that the *H. sabdariffa* fibre improved the tensile and FS while the sisal fibre strengthened the IS. Essentially, Athijayamani *et al*. (2008) reiterated that increasing the quantity of the cellulosic fibres decreases the mechanical properties of the composites. Dikbas *et al*. (2012), who used different forms of E-glass fibres at varying concentrations (2.5%, 3%, 4% and 5%), reported that the IS of denture base acrylic resin increased as the concentration of fibres increased. In light of the aforementioned, it can be concluded that the volume of fibres is directly proportional to the reinforcement of polymer matrices. In terms of the fibre content, fibre size is a contributing factor to the reinforcement of polymer matrices. This is pertinent to this study as fibre size is an underpinning concept and is considered in the research design and methodology of this study. The next section reviews the effect of fibre sizes on the mechanical properties of composites.

2.9 Effect of Fibre Size (Length) in Reinforcement of Polymers

Singha and Thakur (2008b: 789), asserted that fibre size is a critical factor in the reinforcement of composites. In contrast to short fibre (3mm) and long fibre (6mm), they claimed that *H. sabdariffa* fibre with particle size of 200µm more significantly improved the mechanical properties of a urea-formaldehyde based composite. This is consistent with Singha and Thakur (2009a), who showed that in comparison to short and long fibres, the 200µm *H. sabdariffa* fibres significantly improved the strength properties of resorcinol formaldehyde based composites. Concomitantly, Wen (2015: 386) revealed that micro particle size *H. sabdariffa* fibre (200µm) in urea-formaldehyde based composite had a higher load in comparison to short and long fibres. Their work supports Fu *et al*. (2008) that for a given volume of reinforcing material, the mechanical properties increase with a decrease in particle size. They emphasised that smaller particle size reinforcements at a specified volume have a higher surface area because higher mechanical properties are imparted through a more efficient stress transfer than is the case with larger size particles.

Singha and Thakur (2009c) posited that an increase in the mechanical properties of composites may be due to increase in the surface area of fibres and an increased fibre-to-matrix interaction in the composite. They further maintained that increasing the fibre size in a composite, decreased the fibre surface area thereby facilitating more fibre-to-fibre contact. Effectively, and in turn, the interlocking between the fibre and the matrix is reduced. Consequently, the ability of the matrix to transfer load to the reinforcing fibre is reduced considerably, which further reduces the mechanical properties. Furthermore, Singha and Thakur (2009c) contended that the interfacial bond between fibre and matrix in composites is dependent on the surface topology of the fibre as each fibre forms a separate interface with the matrix. In support of their argument, Fuqua *et al*. (2012) emphasised that cellulose in lignocellulosic fibres influences fibre properties and the mechanical performance of fibres in the reinforcement of composites. They posited that cellulose contains a huge quantity of hydroxyl groups (OH) which leads to large hydrogen bonds with the hydroxyl groups of the matrix. These in turn align in an organised method thereby forming a crystalline region to improve the mechanical properties of composites, overall.

In addition, and post their work of reinforcing acrylic resins with different aesthetic fibres, Dogan *et al*. (2008) asserted that 2mm fibre lengths have the highest FS compared to the 4mm and 6mm. Hence, they concluded that an increased fibre length decreases the FS. In conjunction with fibre length, the percentage (%) volume of fibres used must also be considered. This is supported by Xu *et al*. (2013) who showed that fibre length is inversely proportional to fibre % volume used. They revealed that denture base acrylic resins reinforced with 1.5mm and 3mm ramie fibres at 10% and 4% volume, respectively, increased the flexural modulus. Xu *et al*. (2013) pointed out that an increase in the % volume of fibres causes them to agglomerate, thereby weakening the interfacial bond between the denture base acrylic resins and fibres. They therefore advised when using longer fibre lengths that the % volume should not exceed the recommended level of 4%. The work of the aforementioned authors was pertinent to this study. Notwithstanding the above, Biagiotti *et al*. (2004) and Reddy and Yang (2005) asserted that the quality of cellulosic fibres and their effects on the mechanical properties of composites are partly dependent on the method of fibre extraction. This is discussed in the following section

2.10 Methods of Retting of Fibres

According to Tahir *et al*. (2011: 5268), the methods and conditions under which fibres are retted determine the quality of fibres produced. They argued that fibres can be custom-made for specific higher value products such as building structures and car accessories used for various applications. Generally, these higher value products depend on the retting process used to individualise the fibres from the fibre bundles. As noted by Biagiotti *et al*. (2004), the two conventional methods used are field retting (or dew retting) and water retting. Tahir *et al*. (2011) outlined other methods such as enzymatic, mechanical and chemical retting. An explanation on each of the above retting methods follows.

2.10.1 Field/Dew Retting

Field retting is highly dependent on a particular atmospheric condition within a specific geographical location and is a process where plant stalks are left on the ground to decay through the action of aerobic or soil fungi. This causes the pectin and hemicellulose of the plant stems to eventually degrade. From an agricultural perspective, field retting takes several weeks to produce fibres of different qualities and the process is known to contaminate the soil. Biagiotti *et al*. (2004), Holbery and Houston (2006), Tahir *et al*. (2011), and Dhanalaxmi and Vastrad (2013) reported that while field retting produces large amounts of finely sized fibres, the process however produces fibres that are coarse in texture and brown in colour. These physical characteristics adversely impact on the aesthetics of the reinforced materials.

2.10.2 Water Retting

Holbery and Houston (2006: 83) described water retting as stalking the plant stems together and submerging them in water. Other scholars (Biagiotti *et al*. 2004; Tahir *et al*. 2011; Amel *et al*. 2013; Ruan *et al*. 2015) have elaborated that water retting relies on the action of bacteria in the water to putrefy or decompose the pectin. Although water retting takes between seven to ten days to release the fibres from the stalks of the plant stems, the process produces fibres that are long and fine, both in size and texture. For example, Dhanalaxmi and Vastrad (2013), used the “vertical-horizontal soaking and horizontal soaking methods”. They concluded that the vertical-horizontal soaking method produces finer fibres, while the horizontal soaking method produces fibres with improved mechanical properties.

Moreover, Singh (n d) noted that water retting depends on several factors such as: volume of water; temperature and pH level of water; age of plant; and amount of fertiliser used in cultivating the plant. He pointed out that these factors critically affect the retting of fibres, specifically noting that young plants ret quicker than older ones. Plants grown with a high quantity of fertilisers require less time to ret than plants grown without fertiliser. These factors were taken into account in this study.

2.10.3 Enzymatic Retting

Enzymatic retting is a process where commercially or purposely isolated enzymes known as pectinases are deliberately introduced onto the fibrous cellulosic of the stalks of the plant stems in order to break down the pectin and loosen the fibres (Kozlowski *et al*. 2006; Tahir *et al*. 2011). This method emanated from the knowledge that pectinolytic enzymes in plant stalks are critical in the natural retting of plant fibres. In contrast to the longer time periods involved in field and water retting, Bruhlmann *et al*. (2000), Biagiotti *et al*. (2004), and Kozlowski *et al*. (2006) highlighted that enzymatic retting takes between 12 to 24 hours to loosen the fibres from the stalk and to effectively produce fibres that are fine in texture and size. They also clarified that the growth of the plant, along with the bundle shape of the fibres, and the intended use of fibres, are preconditions to the overall enzymatic retting process. In spite of the aforementioned advantages, enzymatic retting is not commonly used due to the high cost and the process of selecting the enzyme.

2.10.4 Mechanical Retting

Biagiotti *et al*. (2004) and Holbery and Houston (2006) have described mechanical retting, which is also known as green retting, as a process where individual fibres from the bundle are loosened through mechanical means such as crushing and hammering. Other authors (Aji *et al*. 2009, Tahir *et al*. 2011, Thomas *et al*. 2011, Fuqua *et al*. 2012, and Amel *et al*. 2013) reported that mechanical retting is simple, fast, produces short fibres and eliminates weather-related preconditions associated with field and water retting. Despite the aforementioned advantages, mechanically retted fibres are coarser than field and water retted fibres, and are therefore mainly used for textiles, paper and fibreboard products.

2.10.5 Chemical Retting

Chemical retting involves extracting the fibres in a heated container using solutions of acids or alkali to dissolve the pectin in the bast. According to Tahir *et al*. (2011), this is an effective method of producing clean and smooth long fibres in a short period. Amel *et al*. (2013: 119) asserted that alkali (NaOH) retting produces high quality fibres as it hydrolyses the amorphous region while ordering the crystalline component, which primarily determines the overall mechanical performance of the fibres. Conversely, and as explained by Holbery and Houston (2006), chemical retting affects the physical properties such as tenacity, colour and lustre of the fibres. Tahir *et al*. (2011) further argued that chemical retting requires high energy to effect the process, which generates waste that is expensive to dispose of. Significantly, when higher amounts of chemicals are used, the tensile strengths of the retted fibres are reduced.

From the foregoing literature review, it can be gathered that no single method of retting of fibres is regarded as providing the optimum result since all methods have their merits and demerits in terms of fibre quality, environmental concerns, and cost. As asserted by Fuqua *et al*. (2012), the procedure adopted in the retting of fibres essentially affects the quality, morphology, surface composition, and mechanical properties of the fibres. Furthermore, Biagiotti *et al*. (2004) and Fuqua *et al*. (2012) noted that cellulose, the primary constituent of bast fibres, is responsible for mechanical performance in composites; cellulose contains both crystalline and amorphous hydrophilic components, which absorb moisture. The hydrophilic nature of cellulosic fibres counters the hydrophobic nature of polymer matrices when they are mixed together. This absorption of moisture enlarges the fibres thereby causing a weak interfacial bond between the two materials. Ultimately, the mechanical properties of composites are lowered (Mohanty, Misra, Drzal 2001; Bhowmick, Mukhopadhyay and Alagisuramy 2012; Kabir *et al*. 2012). Hence, ways of modifying the fibres to effectively reduce their ability to absorb moisture need to be found.

2.11 Fibre Modifications

As mentioned in Section 2.5, the hydrophilic character (high water absorption) and poor wettability properties of cellulosic fibres result in a poor interfacial bond between fibres and matrices. Li *et al*. (2007) argued that using various methods of modifying fibres will help interlock the fibres with the matrices. Thomas and Pothan (2008) therefore advised using specific surface modifications to facilitate an efficient hydrophobic barrier, and to minimise the interfacial energy with a non-polar matrix. For example, and as noted by Paul, Pothan and Thomas (2008) and Kalia *et al*. (2009), chemical modifications of fibres function by galvanising the hydroxyl groups (OH) or introducing new moieties (group of atoms) that can react and interlock with the polymer matrices. Essentially, and as pointed out by Thiruchitrambalam *et al*. (2010), chemical modifications cleanse and increase the exterior unevenness of the fibre surfaces and reduce water absorption. Belgacem and Gandini (2008: 15), however, have cautioned that in order to preserve the integrity of the fibres and their mechanical strength, modifications must be limited to the superficial OH groups. Although Thomas and Pothan (2008), and Fuqua *et al*. (2012) noted other forms of improving fibre properties, this study used chemical modification. The literature documents (Li *et al*. 2007; Fuqua *et al*. 2012; Kabir *et al*. 2012; Saha *et al*. 2015) various methods of chemically modifying fibres such as: alkali treatment (mercerisation), silane coupling, acetylation, benzoylation, graft copolymerisation, maleated coupling, bleaching treatment, and permanganate treatment. Each method is briefly described below.

2.11.1 Mercerisation/Alkali Treatment

Mercerisation is used to chemically treat cellulosic fibres in a solution of alkali materials – either sodium hydroxide (NaOH), potassium hydroxide (KOH), or lithium hydroxide (LiOH), at varied concentrations and different time intervals. Several scholars (Singha *et al*. 2009; Shah *et al*. 2012; Hashim *et al*. 2012; Saha *et al*. 2015) have posited that mercerisation alters the surface topography of fibres, increases fibre wettability, and activates the hydroxyl groups of the cellulose (expressed in the chemical equation below), thus enabling an effective interfacial bond between fibres and matrices. They argued that the material selected for mercerisation depends on the final application of the fibres or composites.

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O} - \text{Na} + \text{H}_2\text{O}$$

(Hashim *et al*. 2012)

Significantly, research work conducted by Modibbo *et al*. (2007), Aji *et al*. (2009), Singha *et al*. (2009), and Saha *et al*. (2015) has shown that mercerisation improves crystallinity, tenacity and strength of the fibres, and decreases the swelling rate, moisture absorbance, and water uptake of cellulosic fibres in solvents. For instance, Fiore, Di Bella and Valenza (2015) revealed that epoxy based composite reinforced with NaOH treated kenaf fibres showed significant improvement in the flexural and tensile strengths. Similarly, Vilay *et al*. (2008) showed that polyester reinforced with NaOH treated bagasse fibres show significant improvement in flexural and tensile strengths when compared against untreated fibres. In particular, there was a higher number of 'pull-out' fibres in untreated bagasse fibres than treated bagasse fibre-reinforced polyester composite. Evidently, and while there were some voids left behind by the 'pull-out' fibres, the treated fibres largely remained implanted together. This finding was pertinent to this study in terms of examining the microstructure of the fracture surface of reinforced denture base acrylic resins.

Rokbi *et al*. (2011) reported that another benefit of mercerisation is the enhanced interfacial bond between the fibres and the matrix. Abral *et al*. (2012) further demonstrated the positive effects of mercerisation of fibres when they treated screw pine with NaOH at different concentrations at a constant time of one hour. They emphasised that treated fibres exhibited significant improvement in mechanical properties in comparison to untreated fibres. Similarly, Jayabal *et al*. (2012) treated husk coir fibre with NaOH at different concentrations and time. They reported an improvement in the mechanical properties of the coir-polyester composite. Equally important, Abral *et al*. (2012) and Kabir *et al*. (2012) have advised against using alkali beyond its maximum concentration and soaking time as this causes excess delignification or damage to the fibres. This has been considered in the mercerisation of *H. sabdariffa* fibres, which is discussed in the methodology chapter.

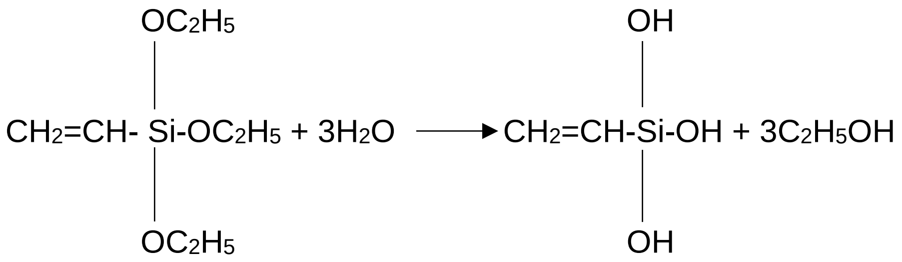
2.11.2 Silane Coupling

According to Li *et al*. (2007: 27), Xie *et al*. (2010: 807), and Fuqua *et al*. (2012: 280 & 281), silane treatment is a process of applying silane based chemicals with double-functional group molecules on the surfaces of fibres. These coupling agents function at the interface by reacting with the fibres and the matrices to bridge the two materials by the formation of covalent and hydrogen bonds. This effectively improves the interfacial bond between the materials. Furthermore, Fuqua *et al*. (2012) pointed out that the choice of silane material in the treatment of natural fibres is dependent on the matrix to be used. As illustrated in the chemical equation below, they further explained that the two-step silane treatment begins with alkalisation of the fibres, which cleans the fibre surfaces and activates the hydroxyl groups.

Step 1 $\text{Fibre-OH} + \text{NaOH} \longrightarrow \text{Fibre} - \text{O} - \text{Na} + \text{H}_2\text{O}$

Sodium hydroxide – fibre reaction (alkalisation)

Step 2



$$CH_2{=}CH\text{-}\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}\text{-}OC_2H_5 + 3H_2O \longrightarrow CH_2{=}CH\text{-}\underset{OH}{\overset{OH}{Si}}\text{-}OH + 3C_2H_5OH$$

Silane hydrolysing in water

(Fuqua *et al*. 2012)

Other scholars (Bilba and Arsene 2008; Yu *et al*. 2010; Kabir *et al*. 2012) have reported that silane coupling leads to the formation of composites with improved properties such as tensile strength, thermal stability, Young modulus, and IS of fibres and composites. Sgriccia, Hawley and Misra (2008) revealed that silane treated kenaf composite absorbed less water with significantly improved FS in comparison with untreated fibre composite. Similarly, Huda *et al*. (2008) and Yu *et al*. (2010) demonstrated the positive effects of silane coupling on poly (lactic acid) (PLA) reinforced with kenaf and ramie fibres respectively. They revealed that the glass transmission temperature, storage modulus, and heat deflection temperature, increased significantly, thereby improving the thermal stability of the composite.

Threepopnatkul, Kaerkitcha and Athipongarporn (2009) also reported improvement in the mechanical properties – Young’s modulus, tensile strength and IS – of the composite reinforced with silane treated fibres. Subsequently, Panyasart *et al*. (2014) showed silane treated pineapple leaf (PALF) reinforced polyamide 6 composite had higher tensile strength and thermal stability due to improved interlocking between the fibre and the matrix. In spite of the reported positive effects of silane treatment on natural fibres, Huda *et al*. (2008) asserted that alkali treatment imparts better IS and facilitates increased removal of impurities from the fibres. This produces rough surface topography, which enhances bonding between the fibres and matrices. This study therefore used mercerisation to treat the *H. sabdariffa* fibres.

2.11.3 Acetylation

Many authors, (Li *et al*. 2007; Fuqua *et al*. 2012; Ahmad *et al*. 2015; Saha *et al*. 2015) described acetylation as a form of esterification treatment to modify cellulosic fibres. This is achieved by introducing acetyl functional (CH_3CO^-) groups to improve the hydrophobicity of the fibres. The process involves generation of acetic by-product (acyl group) to react with the hydroxyl groups (OH) of the fibres to remove the hydrophilism, and increase the fibre stability, which in turn imparts the properties of composites. Mukherjee and Kao (2011) have noted that pre-treatment by mercerisation to expose the surfaces of the fibres enables an effective acetylation process. Kabir *et al*. (2012) pointed out that the sequential use of acetic acid and acetic anhydride enables sufficient reaction with cellulosic fibres. They elaborated that the fibres must be soaked in acetic acid first, and thereafter treated with acetic anhydride to impart a rough surface topography to the fibres. Jacob *et al*. (2005) and Akil *et al*. (2011) cautioned that the by-product of acetic acid must be removed from the surface of the fibres prior to them being used in composites. If not removed, the by-product will prevent interlocking between the matrix and the OH groups of the cellulose, which is responsible for imparting of mechanical properties. Recently, Wang *et al*. (2014) revealed that acetylation reduces hydrophilicity thereby improving and providing a better bonding between fibres and matrices. Consequently, the FS and shear strength of the fibre treated composite improved in comparison with the untreated fibre composite. They reiterated that acetylation causes etching of the fibre surfaces making them unevenly rough which translates to higher fibre contact with the matrix.

Conversely, Jacob *et al*. (2005) and Fuqua *et al*. (2012) have argued that acetylation is not the most effective method of improving the interfacial bond between fibres and matrices. They contended that strong acids used as catalysts in acetylation treatment hydrolyse the cellulose thereby damaging the fibres. The hydrolysis of the cellulose ultimately lowers the thermal stability and properties of composites. Additionally, and as highlighted by Wang *et al*. (2014), hybrid treatment involving acetylation may cause excess removal of lignin and hemicellulose, which is the binder of cellulose in fibres, thereby weakening the fibres and consequently the mechanical properties of composites.

2.11.4 Benzoylation

Li *et al*. (2007), Kalia *et al*. (2009), and Kabir *et al*. (2012) described benzoylation as the application of benzoyl functional groups such as benzoyl peroxide to improve the hydrophobicity of natural fibres and to facilitate the interfacial bond properties. This treatment also improves the thermal stability of the fibres, together with moisture resistance and the mechanical properties of composites. Benzoylation uses alkali pre-treatment to clean the fibre surfaces to expose the reactive OH groups. Essentially, this treatment functions to replace some of the OH groups of the cellulosic fibres thereby improving their adhesion with matrices. Puglia *et al*. (2005) pointed out that the presence of peroxides in the treated fibres effect polarity in the polymer matrix, and the polar groups on the cellulose. Consequently, a reactive group forms that promotes cross linking of polymer chains within the matrix. For example, Murali and Chandramohan (2014) showed that the tensile and impact strengths of reinforced epoxy hybrid-treated (alkalisation, acrylonitrile and benzoylation) hemp fibres were significantly higher in comparison with the untreated fibre composite.

2.11.5 Graft Copolymerisation

Graft copolymerisation introduces high energy radiation free radicals on the fibre surfaces to enhance the interfacial bond between fibres and polymers (Li *et al*. 2007; Kabir *et al*. 2012; Chauhan and Kaith 2012). The free radicals (co-polymers) react with the cellulosic hydroxyl groups to promote contacts of reactive cellulosic radicals to the polymerisation medium. Li *et al*. (2007), and Kabir *et al*. (2012) elaborated that graft copolymerisation presents resilient covalent bonds on the fibre surfaces which in turn improves their moisture resistance and mechanical properties. In an experiment involving copolymerisation of jute fibres, Vilaseca *et al*. (2005) reported that this treatment reduced water absorption rate and the effects of *trichoderma reesei* microorganisms. Similarly, Vilay *et al*. (2008) reported an improvement in the mechanical properties of graft copolymerised bagasse fibre-reinforced polyester composite. Significantly, the fractured surfaces of the untreated composite revealed more fibre ‘pull-out’ with corresponding voids. In contrast, treated composite showed improved interfacial bond between the components as fibres were firmly embedded.

The glass transition temperature (Tg) of the copolymerised composites was higher than untreated composite. Importantly, Chauhan and Kaith (2012) reported that copolymerisation of *H. sabdariffa* fibre increases the chemical resistance thereby preserving the overall properties and longevity of composites. Further, the modulus of rupture and MOE of the composites improved considerably in comparison with that of the untreated composite. More recently, Rosli *et al*. (2015) asserted that copolymerisation of fibres improves thermal stability.

2.11.6 Maleated Coupling

Maleated coupling, like other chemical treatments, is used to modify interaction between fibres, fillers and polypropylene (PP) matrices in order to improve interfacial bond and mechanical properties of composites. Jacob *et al*. (2005) and Fuqua *et al*. (2012) explained that maleic anhydride (MA) groups interact with OH groups of the cellulose fibres to form a bond between MA and oxygen (O_2) of the cellulose. Li *et al*. (2007), Kalia *et al*. (2009), and Kabir *et al*. (2012) however, pointed out that for enhanced mechanical properties to be achieved, an increase in temperature to around 170^{o}C is needed for the MA to be able to interact with the PP chain. In support of the arguments of the aforementioned scholars, Yan *et al*. (2013) reported tensile, FS and IS of treated PP-hemp maleated composite improved by 40%, 47% and 44% respectively. They revealed that the fracture morphology of the untreated fibre composite showed ‘pull-out’ of fibres with long extracts. The treated fibre composite by contrast had fibre breakage and short extracts indicating adhesion between fibres and matrix. Similarly, compared to untreated fibre composite, Catto *et al*. (2014) reported that high density polyethylene reinforced with treated eucalyptus fibres exhibited significant improvement in tensile strength and MOE. This improvement in mechanical properties is supported by the fracture morphology that shows the particles of the fibres adherent to the matrix. The thermal properties of the MA treated high density polyethylene also improved.

2.11.7 Permanganate Treatment

Permanganate treatment involves using a compound containing permanganate group (MnO^{-4}) to form cellulose radicals on the surfaces of fibres through the formation of a manganese ion. This is achieved by the reaction of the permanganate inducing grafting reaction between the fibres and polymer matrices. According to Fuqua *et al*. (2012) and Saha *et al*. (2015), most permanganate treatments utilise a $KMnO_4$ solution. Similar to mercerisation, this treatment roughens the surfaces of natural fibres thereby promoting interlocking between the fibres and matrices. Paul *et al*. (2010) revealed that permanganate treated fibres significantly improve the tensile strength and tensile modulus along with FS and flexural modulus of composites. Despite the positive attributes, Fuqua *et al*. (2012) cautioned that very high concentrations of permanganate degrade cellulosic fibres which in turn adversely affects the mechanical properties of composites. Corroborating Fuqua *et al.*'s findings, Mondal *et al*. (2015) further noted that soaking fibres in $KMnO_4$ for a long period negatively impacts on the fibre properties. They therefore advised that the optimum soaking time is between one to three minutes.

2.11.8 Peroxide Treatment

Peroxide treatment uses a peroxide functional group (ROOR), which has a divalent ion O-O to improve the properties of fibres and composites. The functional group, as outlined by Li *et al*. (2007) and Saha *et al*. (2015), decomposes to free radicals of RO- which in turn react with the activated hydrogen group H^+ of the cellulosic fibres and the matrices. Kabir *et al*. (2012) pointed out that benzoyl peroxide and dicumyl peroxide are the most common chemicals used in peroxide treatment. Li *et al*. (2007), Kabir *et al*. (2012), and Saha *et al*. (2015) noted that peroxide treatments are preceded by alkali pre-treatment and that elevated temperatures are to be used to decompose peroxides to release the radicals. Li *et al*. (2007) also reported that the tensile strength of composites made up of peroxide treated fibres improved because hydrophilicity of fibres reduced, which in turn induced better interfacial adhesion between the fibre and the matrix. Fuqua *et al*. (2012), however, cautioned that the rate of decomposition in peroxide treatment can affect the mechanical properties of composites. Therefore, a comprehensive understanding of the treatment before the commencement of the process is necessary. From the foregoing literature review, it can be gathered that the fibre modification method chosen is predominantly dependent on the fibre concerned, the required applications of the composite, and to some extent the expertise of the operator.

In summary, this chapter has outlined the various denture base materials, particularly acrylic resins, and their ideal requirements as denture base materials. The physical, chemical, biological and mechanical characteristics of acrylic resins are essential to the understanding their clinical acceptance. The literature reviewed also highlighted the poor mechanical properties and efforts made to improve acrylic resins, which is integral to the clinical success of dentures. Furthermore, characterising *H. sabdariffa* fibres in terms of their reinforcement potentials, the numerous fibre retting and the modification methods that can be used to make them compatible with matrices have also been reviewed. Importantly, the choice of fibre retting and treatment methods are dependent on the fibre concerned, required applications of the composite, and the expertise of the operator. The next chapter describes the research design and methodology used in this study.

Chapter 3 – Research Design and Methodology

This chapter describes the quantitative research design and experimental research approach used in this study. These are explained in terms of the preliminary study, the pilot study and the main study. The preliminary study examined the physical, chemical and thermal characteristics of *H. sabdariffa* fibres as a reinforcement material. The pilot study describes the experimental study conducted to determine the fibre size and weight percentage that provides the optimum reinforcement to denture base acrylic resins. This provides guide for the main study. Subsequently, the main study describes the experimental work conducted and analyses the mechanical properties of *H. sabdariffa* fibres as denture reinforcement materials.

3.1 Introduction and Background to the Research Methodology

Observation and deductive reasoning was the basis for this study. The volume of repairs and remake of dentures which break or fracture intra- and extra-orally within a few years of clinical use prompted this study. Goguta *et al*. (2006), Kiilu (2008) and Chen *et al.* (2009) noted that high costs and time are involved in repairing dentures. Furthermore, Tacir *et al*. (2006) and Jaber (2011) argued that although metals are used to reinforce acrylic dentures, they are difficult to apply during the fabrication processes. Synthetic fibres on the other hand, as mooted by Ozen *et al*. (2006) and Tewari *et al*. (2102), have become unpopular in the reinforcement of acrylic prostheses due to associated cytotoxicity in the mouth. As documented in the literature, natural fibres such as *H. sabdariffa* have improved the strength of polymeric materials such as Isotactic Poly Propylene (Junkasem *et al*. 2006), polyester (Thiruchitrambalam *et al*. 2010), bio-epoxy (Chandramohan and Marimuthu 2011), and phenol formaldehyde (Thakur *et al*. 2013). It can therefore be inferred that *H. sabdariffa* fibres could be used to reinforce acrylic resins for dental applications. This study used an experimental research design within a quantitative framework.

Ramadass and Aruni (2009) and Creswell (2014) described quantitative research as an objective method of collecting numerically measured data, which are then statistically analysed to explain and predict outcomes. The fundamental principle of quantitative research is that the data obtained must be tangible, reliable and able to be confirmed. According to Kumar (2014: 143-150), there are various experimental designs such as: after-only experimental design; before-and-after experimental design; control group design; double-control design; comparative design; matched control experimental design; and placebo design. The main study of this research used the control group design. As its name suggests, this design has an experimental group that is exposed to the intervention, while the control group is not. Marczyk, DeMatteo and Festinger (2005) described the experimental approach as being a system of research where the researcher randomly assigns variables to the research subject and seeks to manipulate other factors. By doing this, the researcher assigns groups or conditions to independent variables, while keeping the control constant and measuring them to establish the relationship or effect of such variable(s) on the subjects.

It is worth noting that, and in line with the research objectives outlined in Section 1.5, the preliminary phase of this study focused on the feasibility of using *H. sabdariffa* as a fibre-reinforcement material. In contrast, the main phase of this study examined the suitability of *H. sabdariffa* fibres as a reinforcing material. This aligns to the research objectives in Section 1.6.

3.2 Preliminary Study

This phase was conducted to determine the physical, chemical and thermal characteristics of *Hibiscus sabdariffa* fibre as a reinforcing material. Preliminary work, as argued by Ritchie (2003), enables the identification of variables for inclusion so as to understand the basic principles required to structure the main study. Consequently, the relationship between the variables and the formulation of hypothesis for testing is determined. Equally important, preliminary work determines whether the hypotheses will hold true. The preliminary work for this study is detailed in the subsequent sections.

3.2.1 Preparation of *H. sabdariffa* Fibres

Following the harvest of edible calyces and fruits of the *H. sabdariffa* plants (Hoedspruit, Mopani District of the Limpopo Province in South Africa), the stems of these plants were collected and used. A noteworthy point is that the plant stems are usually discarded as waste following the harvesting of fruits. All stems were thoroughly washed in tap water to remove dirt and soil from the basts' surfaces. The basts were then manually separated from the woody part and further laboratory procedures were conducted in the Chemistry Department at DUT.

3.2.1.1 Retting of the Fibres

Figure 3-1 shows the procedures followed for retting of the fibres. Retting of the fibres involved cutting the basts into smaller sizes of approximately 15cm. This facilitated the placement of the basts in laboratory beakers. The beakers containing the basts were filled with water and subsequently boiled at 100^{o}C for 3 hours. The primary purpose of boiling was to remove ligneous matters and to loosen the fibres thereby easing extracting them from the fibre bundles (Abral *et al*. 2012). Tap water was used for the final rinse and separation of the fibres.

Figure 3-1: Retting of *H. sabdariffa* fibres

3.2.1.2 Scouring and Bleaching of the Fibres

The retted fibres were scoured by boiling in a 3% solution of hydrogen peroxide (H_2O_2) for 45 minutes (Modibbo *et al*. 2009). This was done to remove impurities, pectin, waxes, gum fats and oils from the fibre surfaces while improving fibre colour so that it would not negatively impact on the final colour of the denture acrylic resins. The fibres were then rinsed several times under tap water to remove traces of the H_2O_2 and then air dried at room temperature for 24 hours.

3.2.1.3 Fibre Modification through Mercerisation

As highlighted earlier in Section 2.5, lignocellulosic fibres have poor wettability and are hydrophilic in nature which results in poor interfacial bond between the fibres and the matrices. Hence, *H. sabdariffa* fibres were mercerised to impart an efficient hydrophobic property on the fibres, and to consequently promote adhesion between the fibres and acrylic resin.

H. sabdariffa fibres were mercerised by soaking in 8% aqueous sodium hydroxide (NaOH) at room temperature for 8 hours (Jayabal *et al*. 2012). On completion of the soaking period, the fibres were thoroughly rinsed several times with distilled water and subsequently air dried at room temperature for 24 hours. The fibres were further dried in an oven at 70^{o}C for 24 hours. Mercerisation (NaOH treatment) was done to remove hemicellulose, lignin, pectin, wax and oil coverings on the fibres. This process also cleans the fibre surfaces, and makes them more uniform but rough, reduces fibre diameter thereby increasing the aspect ratio (length/diameter), and ultimately improves the interfacial bond between the fibres and acrylic resin matrix. A noteworthy point is that 8% NaOH ensures that the optimum mercerisation condition is not exceeded. Kabir *et al*. (2012) pointed out that a higher concentration of alkali treatment beyond the optimum condition increases delignification. This significantly damages the fibres and reduces their mechanical properties.

3.3 Characterisation of *H. sabdariffa* Fibres

Sandrolini and Franzoni (2010), and Schueremans *et al*. (2011) advise that to understand the properties of materials requires ascertaining their behaviour and compatibility before use. It is therefore imperative to understand the physical, chemical functional groups, and the thermal properties of *H. sabdariffa* fibres to ascertain its potential as a reinforcing material for denture base acrylic resins. Table 3-1 provides an overview of the characterisation tests conducted. A point deserving mention is that these tests were carried out pre and post *H. sabdariffa* fibre modification. This was done in order to determine any changes within the fibres as a result of the modification process.

Table 3-1: Overview of physical, chemical and thermal characterisation tests

Test(s)	Details
Fibre Diameter	The diameter of the *H. sabdariffa* fibres was determined.
Fibre Morphology and Cross section	The shape and structural features, and the arrangement of cells within the *H. sabdariffa* fibres were assessed.
Fibre Density	The weight of *H. sabdariffa* fibres and subsequently the effect on the composite was evaluated.
Moisture Content	The quantity of water in the *H. sabdariffa* fibres was determined.
Moisture Absorption	The water absorption behaviour of *H. sabdariffa* fibres and its effect on the composite was ascertained.
Chemical Functional Groups	The functions of each chemical group of *H. sabdariffa* fibre and their effects on reinforcement of polymers.
Thermal Analysis	The effect of heating on the stability of *H. sabdariffa* fibres and effects on reinforcement of polymers.

3.3.1 Diameter of *H. sabdariffa* Fibres

The diameter of the untreated and treated *H. sabdariffa* fibres were analysed using a field emission scanning electron microscope (FE-SEM, Ultra Series®) (Carl Zeiss, GmbH). Prior to the FE-SEM analysis, the surfaces of the samples were sputtered with a thin layer of gold. This was done to ensure good conductivity of the materials and to prevent accumulation of electrostatic charge. The FE-SEM operated at 5 kV under controlled atmospheric conditions. FE-SEM analysis were conducted by the technician of the microscopic and micro-analysis unit in University of KwaZulu-Natal (UKZN), Westville Campus.

As presented in Table 3-2 and in Figures 3-2 and 3-3, the diameter range of treated *H. sabdariffa* fibres confirms that mercerisation effectively reduces the hemicellulose and lumen size thereby reducing the diameter. In turn, the surface area improves and aspect ratio increases. This result is consistent with Sonia and Dasan’s (2013) finding that mercerisation reduces the diameter of *H. sabdariffa* fibres. From a dental laboratory perspective, it can be inferred that treated *H. sabdariffa* fibres must be treated prior to their use as reinforcement material.

Table 3-2: Physical properties of tested *H. sabdariffa* fibres

H. sabdariffa fibres	Fibre diameter (µm)	Fibre density (g/cm^3)	Moisture content (%)	Moisture absorption (%)
Untreated	42 - 90	1.38	9.8	169
Treated	30 - 73	1.43	7.8	109

3.3.2 Morphology and Cross Section of *H. sabdariffa* Fibres

The morphology and cross section of the treated and untreated *H. sabdariffa* fibres were evaluated using FE-SEM (Ultra Series® Carl Zeiss, GmbH) analysis to determine the shape and structural features, and the arrangement of cells within the fibres, respectively. The surfaces of the samples were sputtered with a thin layer of gold. The FE-SEM operated under controlled atmospheric condition at 20 kV for the evaluation of the fibre morphology, and at 5 kV for the assessment of the cross section. The microscopic examination was done by the technician of the microscopic and micro-analysis unit of UKZN (Westville Campus) and the researcher analysed the morphology and cross section.

Figures 3-4(**A**) and (**B**) present the FE-SEM morphology of untreated and treated *H. sabdariffa* fibres, respectively. As can be seen from Figure 3-4(**A**), untreated *H. sabdariffa* fibres consists of a structural network of bundles of fibres held together by lignin, wax and hemicellulose. Impurities and debris are also present on the smooth surfaces of the fibres. In contrast, Figure 3-4(**B**) shows clean yet rough, fibre surfaces. Although mercerisation removes wax, oil, impurities and debris from the fibre surfaces, the treatment roughens and makes the fibre surfaces uneven. This is critical to promote interfacial adhesion between the fibres and polymer matrix during denture fabrication. These results support the work of Aziz and Ansell (2004) and Sampathkumar *et al*. (2012).

As shown in Figure 3-2**,** the untreated fibres are bundled together by non-fibrous materials and there are hollow structures, which represent lumen, in the *H. sabdariffa* fibres. The lumen size in the treated *H. sabdariffa* fibres (Figure 3-3) is narrower, which indicates that wax, oil, surface impurities and debris have been removed thereby shrinking fibres. Inevitably, the reduction in lumen size reduces the diameter of the fibres, which ultimately increases the aspect ratio. This finding is consistent with Baley *et al*. (2006), Thamae and Baillie (2007) and Vilay *et al*. (2008). A noteworthy point is that improved mechanical properties are achieved through a better load sharing between the fibres as a result of the increased aspect ratio.

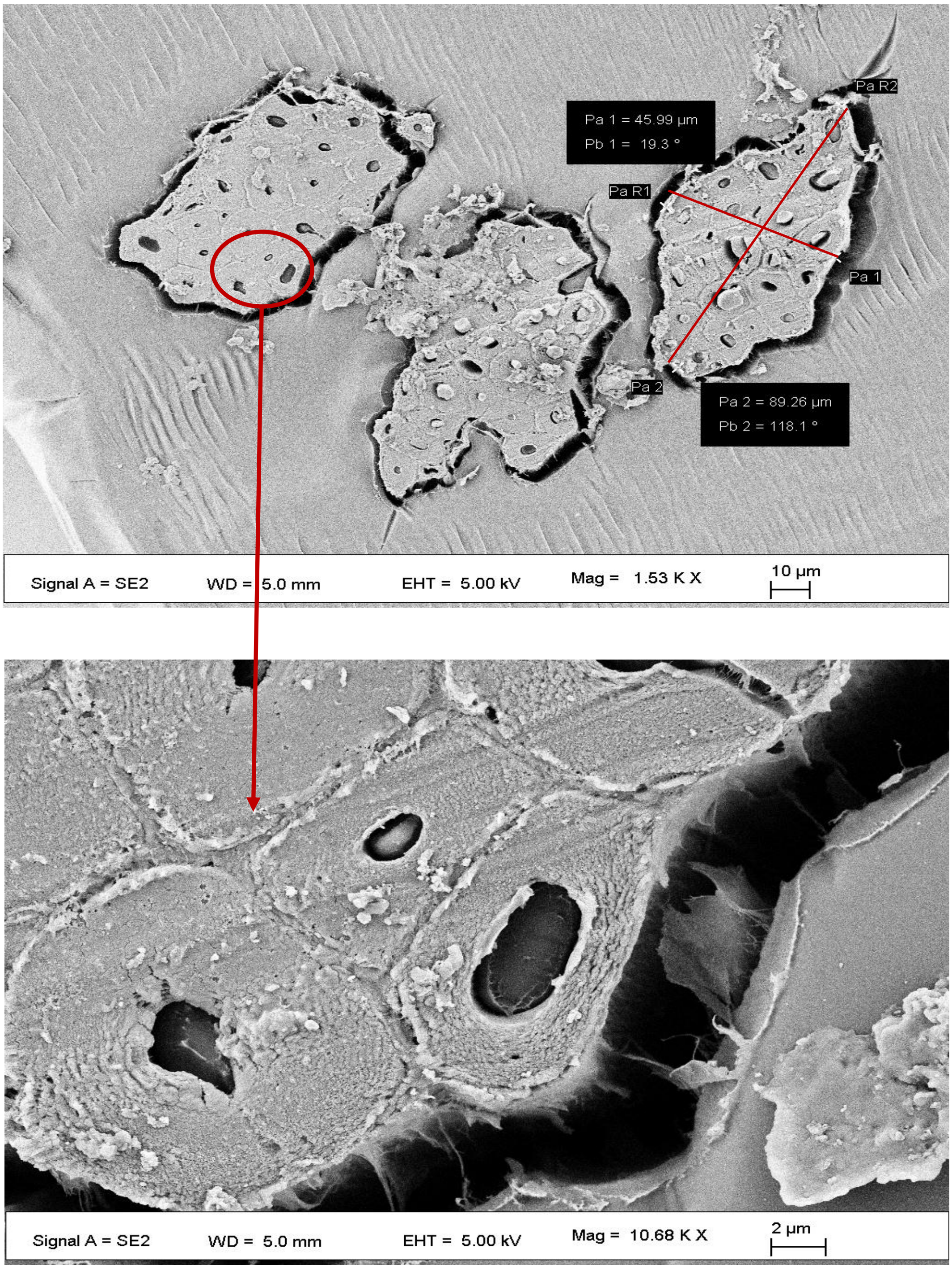


Figure 3-2: Cross-sectional view of untreated *H. sabdariffa* fibres

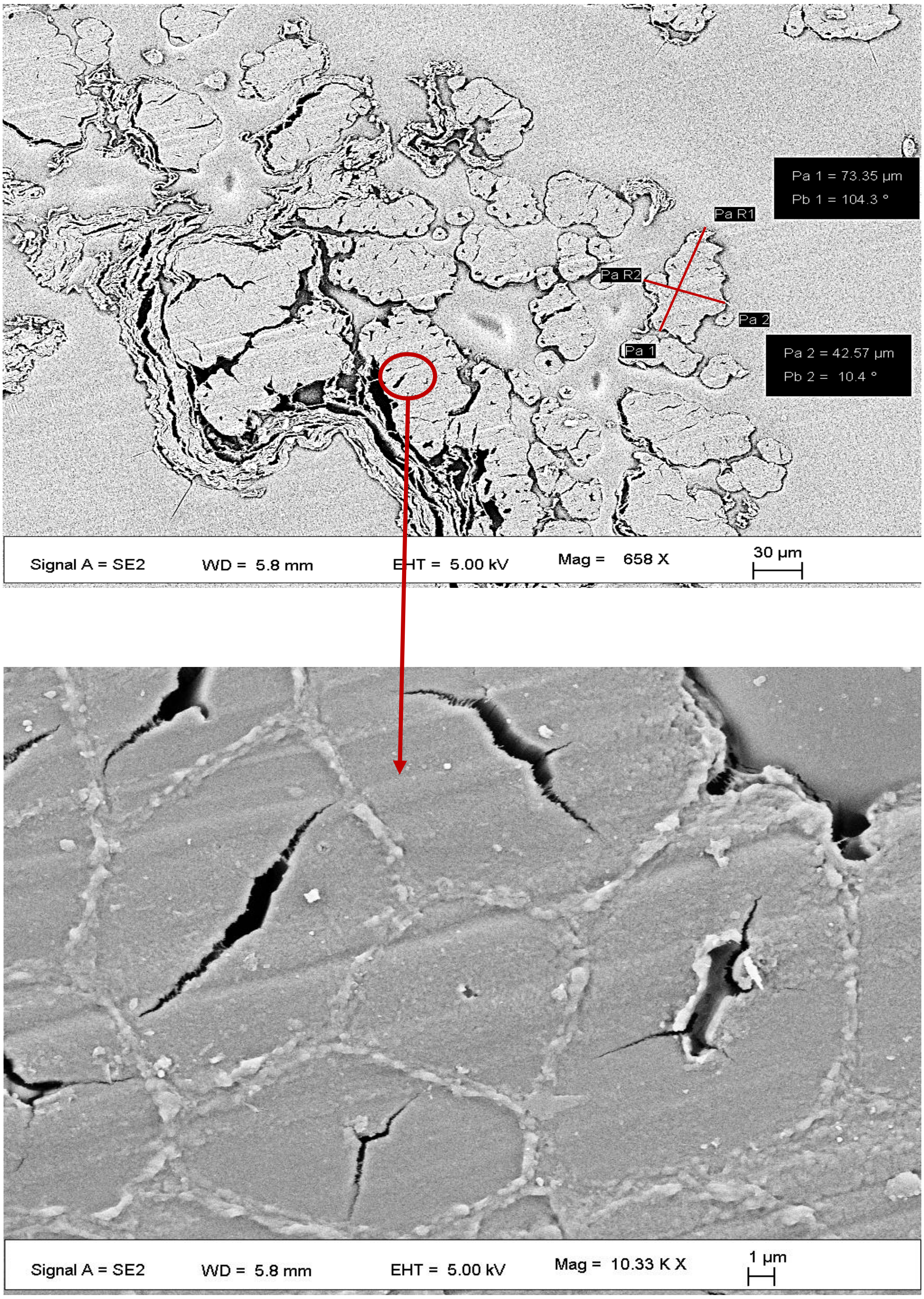


Figure 3-3: Cross-sectional view of treated *H. sabdariffa* fibres.

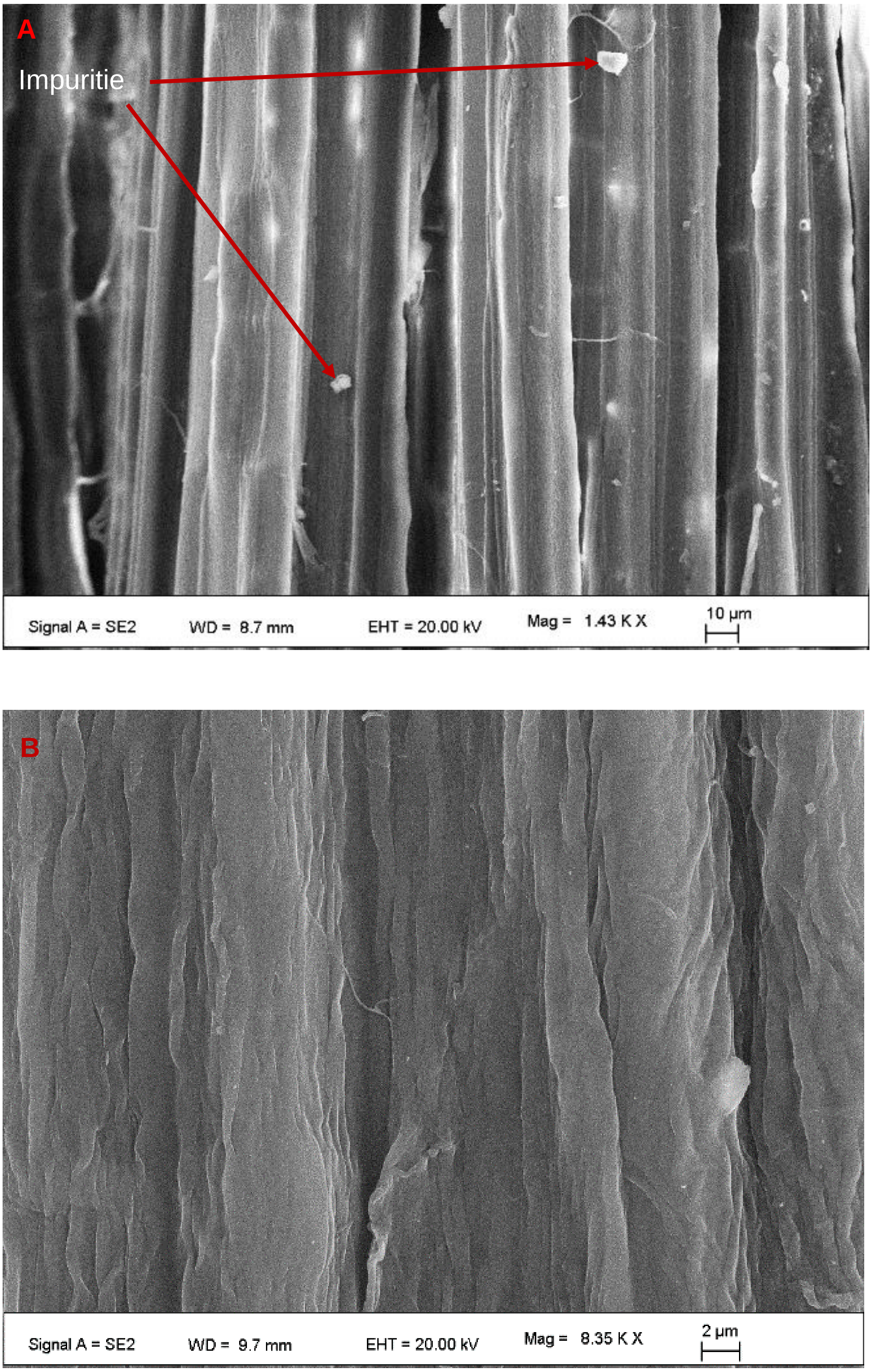


Figure 3-4: Surface morphology of *H. sabdariffa* fibres: (A) untreated; (B) treated

3.3.3 Density of *H. sabdariffa* Fibres

The density of *H. sabdariffa* fibres were determined using Equation 1.

$$\textbf{Density} = \frac{\text{Mass } (M2 - M1)}{\text{Volume } (V2 - V1)} \text{ in gm/cm}^3 \qquad \textbf{(1)}$$

Furthermore, and based on Archimedes' principles, the following steps were applied when determining fibre density:

Step 1: The weight of the container was first determined (M_1) and then immersed in a specific volume of water in a calibrated transparent measuring glass tube.

Step 2: The volume of water displaced was determined (V_1).

Step 3: The container was then filled with ground *H. sabdariffa* fibres and the weight determined (M_2).

Step 4: The container filled with the fibres was then immersed in the specific volume of water used in **Step 1**. The volume of water displaced was determined (V_2).

As presented in Table 3-2, the density of treated *H. sabdariffa* fibres was 0.05g/cm^3 higher than the untreated fibres. This increase in density may be attributed to mercerisation which removes wax, oil and other deposits from the fibre surfaces. Equally significantly, the SEM images (Figures 3-3) highlight narrower lumen structures thereby confirming that fibre modification through mercerisation increases the density of fibres. These results support the work of several other authors (Aziz and Ansell 2004; Modibbo *et al*. 2009; Suardana, Piao and Lim 2010; Nadlene *et al*. 2015 and Razali *et al* 2015). Notably, the density of *H. sabdariffa* fibres is within the range of other reinforcing natural fibres (Table 2-4), which suggests that it can be used to reinforce denture base acrylic resins.

3.3.4 Moisture Content of *H. sabdariffa* Fibres

As recommended by Ichetaonye *et al*. (2015), the moisture content of the fibres was determined using Equation 2. The average moisture content of *H. sabdariffa* fibres in replicates of five was recorded. The five fibre replicates were each weighed using a digital balance [Adam® Equipment S.A. (Pty) Johannesburg, South Africa] with an accuracy of 0.001g and recorded (M_1). They were then placed in an oven at 100°C for 24 hours. Subsequently, the five fibre replicates were removed, reweighed and recorded. They were reheated and further weighed at intervals of two hours until no further change was noticed (M_2). The moisture content was calculated as the percentage of the weight loss.

$$\textbf{Moisture content} = \frac{M1 - M2}{M1} \times 100 \quad \text{in } \% \qquad \textbf{(2)}$$

3.3.5 Moisture Absorption of *H. sabdariffa* Fibres

As advised by Razali *et al*. (2015), the percentage of moisture absorption was determined using Equation 3. The average moisture absorption percentage of *H. sabdariffa* fibres in replicates of five samples was recorded. The *H. sabdariffa* fibres were weighed (M_1) using a digital balance (Adam® Equipment S.A. [Pty] Johannesburg, South Africa) with an accuracy of 0.001g and recorded. Following this, the *H. sabdariffa* fibres were completely submerged in a beaker of de-ionised water at room temperature for 24 hours. *H. sabdariffa* fibres were then removed, drained of excess water and reweighed (M_2) within 60 seconds of their removal from water.

$$\textbf{Moisture absorption} = \frac{M2 - M1}{M1} \times 100 \quad \text{in } \% \qquad \textbf{(3)}$$

There was a 20.4% reduction in the moisture content of mercerised *H. sabdariffa* fibres (Table 3-2). This confirms that hemicellulose, which retains water, was removed from the fibres. This result corroborates Thamae and Baillie (2007), Faruk *et al*. (2012) and Alam *et al.* (2015) that mercerisation fundamentally reduces moisture content and rate of moisture absorption by natural fibres. Importantly, the moisture content of *H. sabdariffa* fibres compares favourably with other lignocellulosic fibres in Table 2-4. It can therefore be deduced that *H. sabdariffa* fibres can reinforce denture base acrylic resins.

In addition, and in contrast to the untreated fibres, there was a 36% reduction in the moisture absorption rate of treated *H. sabdariffa* fibres. The removal of hemicellulose, wax and oily substances from the raw fibres through mercerisation could have caused the water absorption rate to be reduced. This supports the argument of Thiruchitrambalam *et al.* (2010), and Dixit and Verma (2012) that untreated natural fibres have a higher moisture absorption rate because of the hemicellulose. Significantly, and as illustrated in Figure 3-3, mercerisation shrinks the lumen structure of natural fibres by compacting the cell walls and ultimately imparts hydrophobicity to the fibres. In turn, an effective bond between polymers and reinforcing fibres is promoted. This is consistent with the results of Aziz and Ansell (2004) and Kabir *et al*. (2012). The result further suggests that mercerising *H. sabdariffa* fibres is a prerequisite to their use in reinforcing denture base acrylic resins.

3.3.6 Chemical Functional Groups of *H. sabdariffa* Fibres

Fan, Dai and Huang (2012) highlighted that Fourier transform infrared spectroscopy (FT-IR) is an effective way of identifying the structure and functional groups of cellulosic materials. FT-IR analyses the hydrogen bonds and shows the relationship between the various bonds. Moreover, FT-IR correlates the relationship between the physical and the mechanical properties of cellulosic materials. The FT-IR analysis was performed in order to identify the structure and functional groups of *H. sabdariffa* fibres. This was to confirm the presence of hydroxyl (OH) groups in the fibre, which are responsible for the bonds with the hydroxyl (OH) groups of polymeric materials. A Perkin Elmer Universal spectrometer in the frequency of 4000 cm^{-1} to 380 cm^{-1}, operating in attenuated total reflectance (ATR) mode was used to conduct the FT-IR analysis. Prior to sample analysis, a background study of the process was carried out. Following this, a small quantity of the fibres was placed on the sample holder for analysis. The technician in the Chemistry Department (UKZN, Westville Campus) conducted the the FT-IR analyses. The researcher interpreted and analysed the results.

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The FT-IR spectra of untreated [Figure 3-5(**A**)] and treated [Figure 3-5(**B**)] *H. sabdariffa* fibres were measured in ATR mode in the frequency of 4000 cm^{-1} to 380

cm^{-1}. The spectra showed typical transmittance bands of the various components of lignocellulosic corresponding to cellulose, hemicellulose and lignin. These components are mainly composed of oxygen containing functional groups, alkanes and aromatic groups.

In contrast to the untreated fibres, the spectrum in Figure 3-5(**B**) showed a prominent peak at 3328 cm^{-1} which is associated with hydrogen bonded O-H stretching of cellulose. Hydroxyl based materials are usually detected in the region of 3400 cm^{-1} to 3300 cm^{-1}. The peak at 2901 and 1598 could be attributed to C-H stretching bend of cellulose and C=C stretching of the aromatic ring of lignin, respectively. This supports the work of several authors (Obi *et al*. 2012; Sonia and Dasan 2013; Benyahia *et al*. 2013; Bezazi *et al*. 2014; Teli and Jadhav 2016). The peak observed at 1421 cm^{-1} can be ascribed to CH stretching while the 1368 cm^{-1} can be associated with C-H bending stretch of cellulose. In addition, the transmission peaks of 1157 cm^{-1} and 1027 cm^{-1} can be linked with asymmetric stretching of C-O-C of lignin and C-O stretching of polysaccharides in cellulose, respectively. This result corroborates Liu *et al*. (2009a), Sonia and Dasan (2013), and Benyahia *et al*. (2013). The peak observed at 895 cm^{-1} could be linked with the presence of β glycosidic linkages between monosaccharides of cellulose. The peaks occuring at 657 cm^{-1} and 554 cm^{-1} can be associated with the out of plane vibrations of ring structure and C-OH stretching. This result compares favourably to the findings of De Rosa *et al*. (2010) and Bezazi *et al*. (2014).

Furthermore, and unlike the shift of the peaks 2178 cm^{-1} to 2004 cm^{-1} and 1421 cm^{-1} [2181 cm^{-1} to 2022 cm^{-1} and 1425 cm^{-1} in Figure 3-5(**A**)], there was a disappearance of C=O stretching peak of hemicellulose at 1726 cm^{-1} and a decrease in the intensity of the peak at 1246 cm^{-1} in treated fibres. This confirms that mercerisation significantly removes hemicellulose. Moreover, the intensity of the transmittance peak of 3328 cm^{-1}, the elimination of peak 3908 cm^{-1} and the shift in the peak of 3790 cm^{-1} indicate that the cellulose structure changed. This correlates to the work of several authors (Baley *et al*. 2006; Obi *et* al. 2012; Sonia and Dasan; Benyahia *et al*. 2013; Teli and Jadhav 2015), particularly with regards to mercerisation removing non-cellulosic materials while changing the structure of cellulose. It can therefore be inferred from the FT-IR results that the OH groups of the *H. sabdariffa* fibres were activated to facilitate interfacial bonding with the polymer matrix.

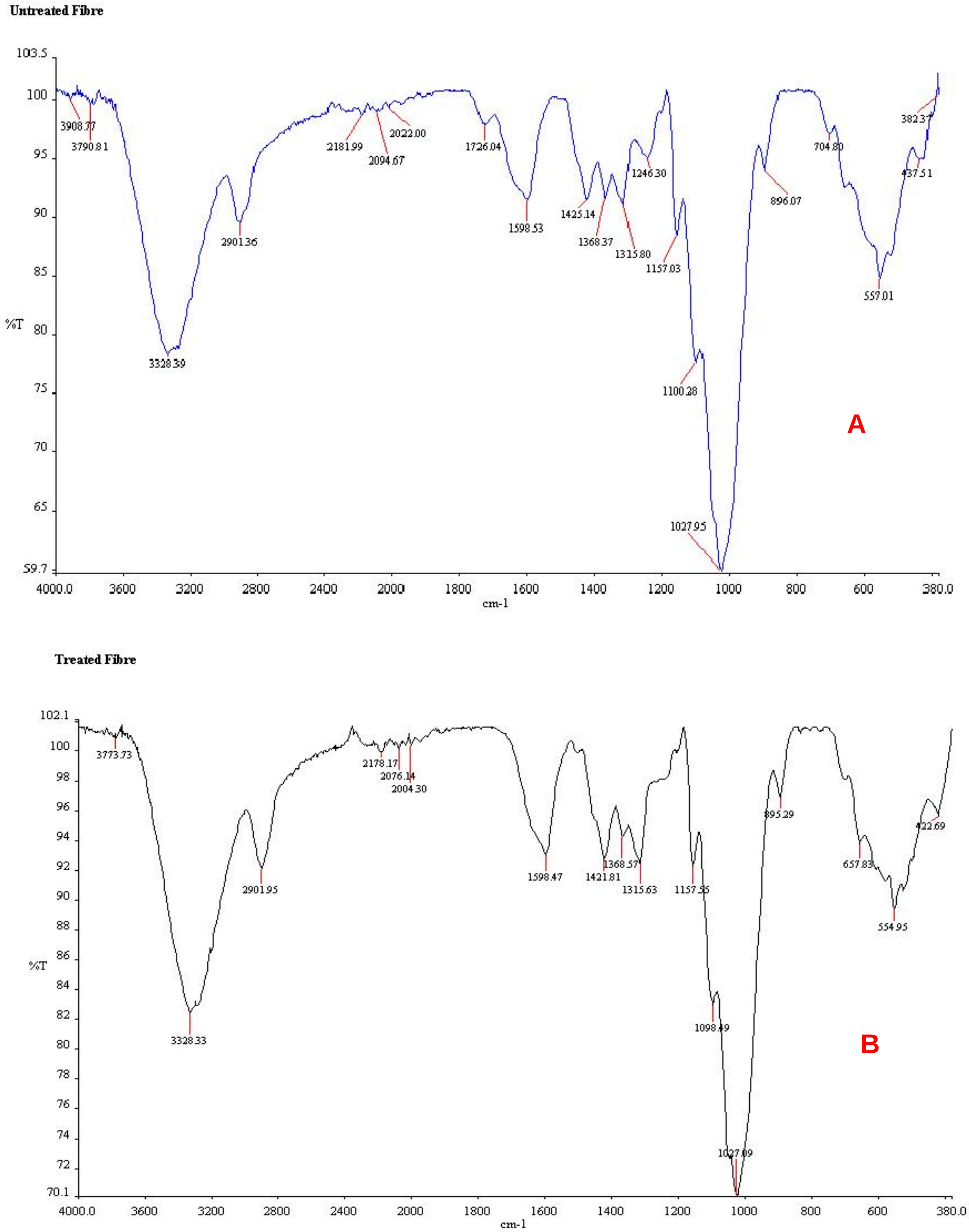


Figure 3-5: FT-IR (ATR) spectra of *H. sabdariffa* fibres: (A) untreated; (B) treated

3.3.7 Thermal Characterisation of *H. sabdariffa* Fibres

De Rosa *et al*. (2010: 117) revealed that a drawback to using lignocellulosic fibres in the reinforcement of polymeric materials is their poor thermal stability. Similarly, Singha and Thakur (2008a) and Razali *et al*. (2015) asserted that in order to ensure high quality polymeric composites, and to avoid the degradation of natural fibres at elevated temperature during manufacturing processes, thermogravimetric analysis is necessary to confirm compatibility of the components. The thermal properties and degradation of *H. sabdariffa* fibres was evaluated using a thermogravimetric analyser (TGA) SDT Q600 series (TA Instruments, Delaware, USA) under dry nitrogen gas flow at the rate of 100ml/min with temperature range of 20^{o}C to 600^{o}C at a heating rate of 10^{o}C/min. The results were analysed using TA Instruments Universal Analyser software. The thermogravimetric analysis was conducted by the technician of the Mechanical Engineering Department in DUT and the interpretation was done by the researcher.

In contrast to Figure 3-6(**A**), the TGA curves in Figure 3-6(**B**) present two thermal events within the temperature range of 40^{o}C to 800^{o}C. The first thermal event at 42 ^{o}C can be attributed to the evaporation of moisture and volatile extractives from the fibres. Consequently, there was a weight loss of about 6.9%, which could be attributed to the reduction of free hydroxyl groups from the fibres. The final thermal degradation noticed between 300^{o}C to 400^{o}C was the decomposition of cellulose. This compares with the work of Teli and Jadhav (2016) that the thermal stability of fibres improved due to mercerisation. Significantly, Figure 3-6(**B**) confirms that mercerisation reduces the hemicellulose content, which accounts for the low water content of the *H. sabdariffa* fibres. The char content of 28.9% further supports the reduction of hemicellulose and water. This is consistent with Obi *et al*. (2012) and Sonia and Dasan (2013). Ultimately, this increased the final degradation temperature, which effectively improved the thermal stability of the treated fibres. The water content result in Table 3-2 further supports this.

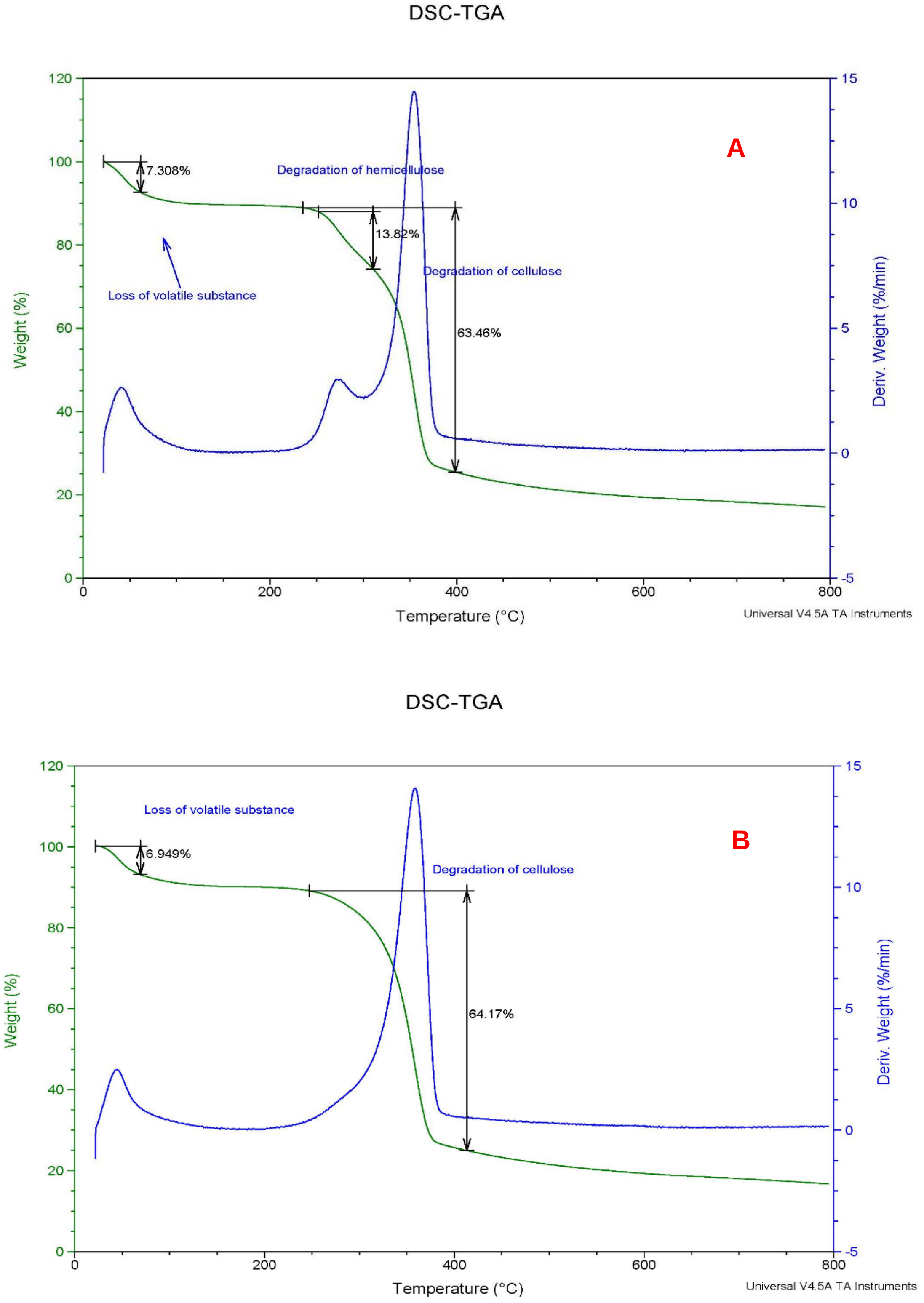


Figure 3-6: TGA curves of *H. sabdariffa* fibres: (A) untreated; (B) treated

3.3.8 Sizing of the Fibres

The treated fibres were chopped into 6mm long fibres, (Figure 3-7**A**), and 3mm short fibres (Figure 3-7**B**). A verneer calliper was used to check the fibres randomly to ensure that the fibres were within the selected measurements of 6mm and 3mm. The 300 µm particle sized fibres (Figure 3-7**C**) were ground and sieved using a mesh (Labotec® sieving mesh: SABS 197- 1971) (Figure 3-8). The treated fibres were subsequently stored in desiccators ready for use.

A – Long fibres **B – Short fibres** **C – 300µm fibres**

Figure 3-7: Different fibre sizes

Figure 3-8: 300 µm Labotec® sieving mesh

3.4 Pilot Study

3.4.1 Preparation of Specimens

Following the ADA Specification No. 12, which is an adapted version of ISO 1567: 1999 for denture base materials, rectangular metal die specimens of 60mm x 10 mm x 3mm and 50mm x 10mm x 3mm (length, width and thickness) for FS test and IS test were fabricated respectively. The metal dies [Figure 3-9(**A**)] ensured that consistent moulds were formed during the flasking and packing process. According to Rawls (2013: 476), flasking is the process of embedding a wax pattern in a gypsum product (dental plaster) enclosed within a denture flask prior to polymerisation. The following steps detail the flasking of acrylic specimens:

- Metal dies were lubricated with Vaseline for easy removal from the dental plaster moulds.
- The dies were invested in a plaster mould in one half of the denture flask using the conventional denture flasking procedure. Mixing of plaster was done according to the manufacturer's instruction on mixing ratio and time.
- Following the setting of the dental plaster, the surfaces of the mould were coated with separating medium (Vertex™ Divosep liquid). The second half of the denture flask was placed in its position and filled with dental plaster.
- Once the plaster mould was set, the denture flasks were opened using a plaster knife. The metal dies were carefully removed so as to avoid any damage to the plaster moulds [Figure 3-9(**B**)].
- The mould cavity and all dental plaster surfaces were then cleaned and coated with the separating medium. As noted by Rawls (2013) the separating medium prevents direct contact and adhesion between the acrylic resins and the plaster mould. The separating medium also prevents water and dissolved polymer or free monomer from soaking into the mould surfaces.

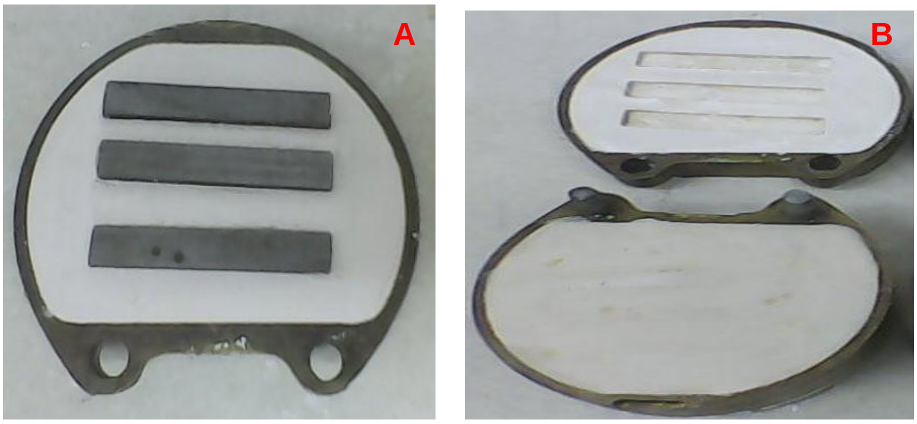


Figure 3-9: Metal dies investment process

(A) Rectangular dies invested in denture flask
(B) Mould ready for packing

3.4.2 Fabrication of Specimens and Sample Size

As illustrated in Table 3-3, there were four sample groups namely, 6mm; 3mm, 300µm and unreinforced. Each sample group had 40 *H. sabdariffa* fibre-reinforced acrylic specimens with four different fibre weight percentages (wt%) while the unreinforced sample group had 10 specimens. An Adam® digital balance (Adam Equipment S.A. [Pty] Johannesburg, South Africa) was used to weigh the fibres. Although the manufacturer's guidelines recommend using a mixing ratio of 0.33ml of Vertex™ (Vertex Dental BV, Zeist, The Netherlands) heat-cure monomer to 1g of Vertex heat-cure polymer, this ratio was adjusted to 0.60ml of monomer for the fibre-reinforced groups only. This ensured complete wetting of the fibres within the mix. In contrast to the mixing ratio used for the fibre-reinforced specimens, the heat-cured acrylic resins mix for the unreinforced specimens was done according to the Vertex™ manufacturer's guidelines.

Table 3-3: Total number of specimens

Sample group	**wt% of *H. sabdariffa* fibres**				**No. of specimens**
	2.5	**5**	**7.5**	**10**	
6mm fibre	10	10	10	10	40
3mm fibre	10	10	10	10	40
300µm	10	10	10	10	40
unreinforced					**10**
	n =				**130**

Generally, the specimens were prepared as follows:

- The pre-determined fibre wt% for each sample group were soaked in 18ml monomer in a mixing closed vessel for 10 minutes. This wetting of the fibres facilitates better adhesion between the fibres and denture acrylic resins.
- The polymer (30g) was mixed with the monomer containing the fibres and thoroughly stirred to ensure random distribution of the fibres and a homogenous mix of the resin.

- When the mixture reached the dough stage (15 minutes), it was then kneaded and placed into the moulds. This is termed “packing” [Figure 3-10(**A**)].
- The second half of the denture flask was carefully replaced to close the flasks for bench pressing. Pressure was slowly but incrementally applied until the flasks had a metal to metal contact of the edges.
- Following the manufacturer’s instruction, the clamped flasks [Figure 3-10(**B**)] were placed in a hot (100°C) Mestra M-9™ curing unit (Mestra, Sondika-Bilbao, Spain) for polymerisation. This process, which is schematically represented in (Figure 3-11), was completed in 20 minutes.
- Denture flasks were removed from the curing bath and when cooled they were opened and specimens were gently removed from the mould.
- All specimens were trimmed using a tungsten carbide bur (Cross-cut, coarse-ISO No. 500104237065; Bredent GmbH & Co KG) at 18000 rpm, and smoothened using Silicon carbide abrasive paper (CC768; Deer Abrasives).

Importantly, and as shown in Figure 3-12, the dimensions of the specimens were maintained post the trimming and finishing processes. It must be noted that specimens were not polished as this process further reduces the dimensions of specimens. A Vernier calliper was used to measure three different areas within each plane of the specimens to confirm uniformity of dimensions. Specimens with defective dimensions, porosity and surface irregularities were excluded.

Figure 3-10: Packing processes

(A) Packing of acrylic resin dough into mould
(B) Clamped denture flasks ready for curing

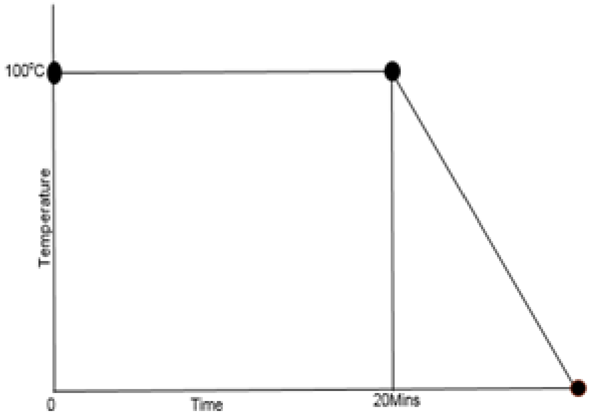


Figure 3-11: Curing cycle

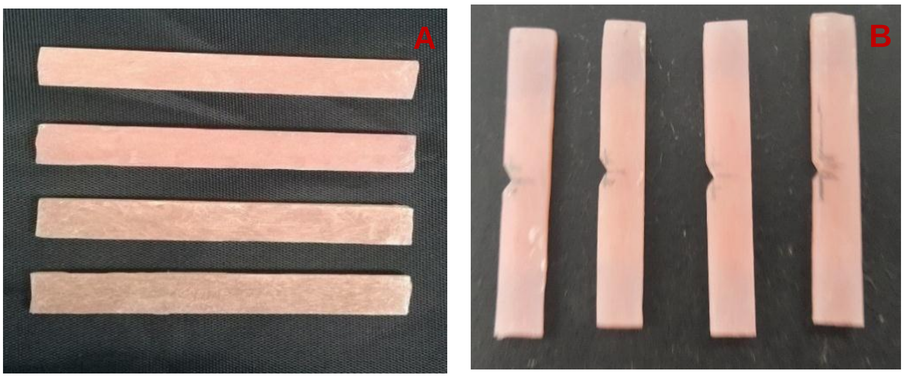


Figure 3-12: Processed denture base acrylic resin specimens

(A) Specimens for flexural testing
(B) Notched specimens for impact testing

3.4.3 Mechanical Testing of Specimens

In order to facilitate flexural and impact testing, each sample group of *H. sabdariffa* fibre-reinforced and the unreinforced acrylic specimens were further divided into two groups. As presented in Table 3-4, each mechanical testing group (n = 65) had 20 specimen representatives of the four different fibre wt% and five unreinforced specimens.

Table 3-4: Number of specimens per mechanical testing group

Sample Group	Weight % of *H. sabdariffa* fibres				No. of Specimens
	2.5	5	7.5	10	
6mm fibre	5	5	5	5	20
3mm fibre	5	5	5	5	20
300µm	5	5	5	5	20
Unreinforced					**5**
	n =				**65**

To simulate the frenal areas where the pressure points are high and the integrity of acrylic resin dentures are most compromised in the oral cavity, specimens were prepared with a 2 mm v-notch at their centres prior to impact testing. McNally *et al.* (2006: 95) advised placing a v-notch as this concentrates the stress and overcomes the effects of surface defects. Following ISO 1567, and prior to mechanical testing, all specimens were conditioned in distilled water at 37°C for 72 hours. This is also in line with ASTM (American Society for Testing and Materials) D 790 and D 256, where test specimens should be conditioned for a period not less than 40 hours prior to testing. Moreover, the conditioning of specimens at 37°C simulates the intra-oral conditions at normal body temperature (Yoshida *et al*. 2016).

3.4.3.1 Flexural Testing of Specimens

Following the ASTM D 790 method of testing, a three point bending on a Lloyd™ LR 30K machine (Lloyd Instruments Ltd; West Sussex, UK) (Figure 3-13) was used to test the FS of the 65 specimens. The distance between the two jig supports was 50mm. The machine was set to provide a cross head speed of 5mm/min and the force applied was located at the centre of the specimen until fracture occurred. The maximum force applied was recorded by the computer software attached to the Lloyd™ LR 30K machine. The data obtained was used to calculate the FS using Equation 4, where the average values are reported in the next chapter.

Flexural Strength = $3FL/2bh^2$ (MPa) ***(4)***

Where F = maximum force or load (N) exerted
L = distance (mm) between supports
B = width (mm) of specimen
H = height or thickness of specimen prior to water storage

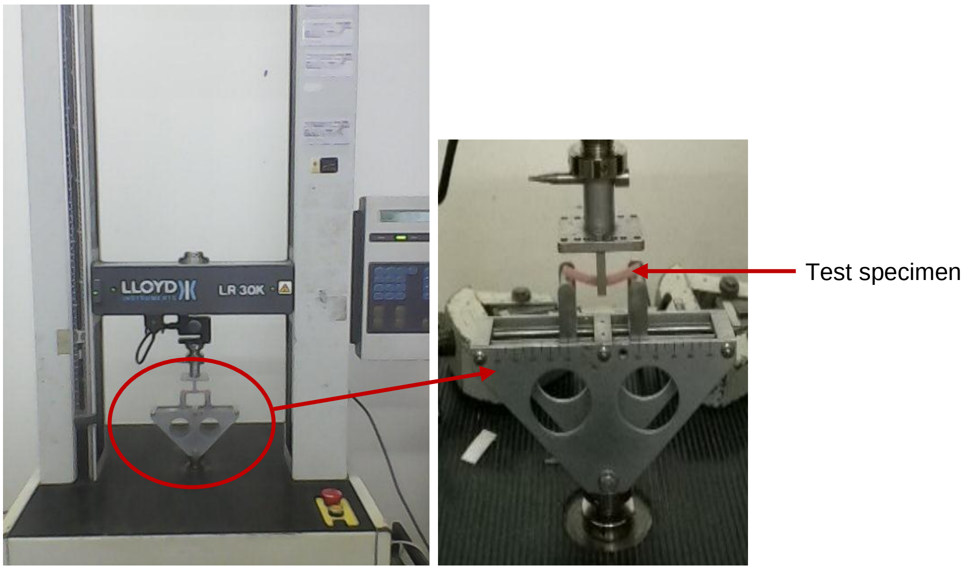


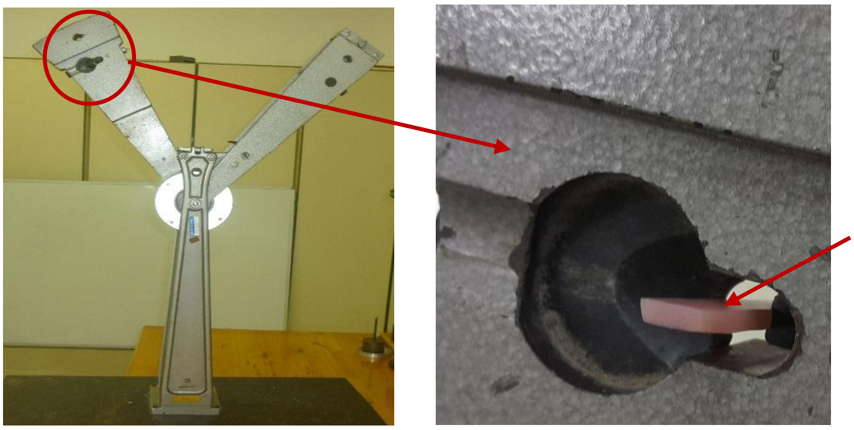
Figure 3-13: Flexural testing of specimen

3.4.3.2 Impact Testing of Specimens

In line with ASTM D 256 method, a Hounsfield™ charpy impact tester [Tensometer Ltd; Croydon, England (Figure 3-14)] was used to test the IS of the 65 specimens. The machine was set to provide a test pendulum with an impact force. The distance between the two fixed jig supports was 50mm. Using Equation 5, the charpy IS of the notched specimens was calculated from the data obtained.

Impact Strength = $AE/T \times W$ (KJ/m^2) ***(5)***

Where AE = absorbed energy
T = thickness of specimen
W = remaining width at the notch of specimen



V-notched specimen ready for Impact test

Figure 3-14: Impact testing of specimen

3.5 Statistical Analysis

Numerical data obtained from the tests were analysed using the Statistical Package for Social Science (SPSS) (Version 23®, SPSS Inc. Chicago, Illinois). Both descriptive and inferential statistics, particularly the one-way analysis of variance (ANOVA), was used to compare the mean strengths of the different *H. sabdariffa* fibre-reinforced and unreinforced specimens. According to Willis (2004: 136), ANOVA identifies the mean differences of values and tests for significant differences between more than two variables ($p < 0.05$). Furthermore, a multivariate test (multiple comparison) was performed using Bonferroni to examine the pairwise differences in the various sample groups.

In summary, the physical, chemical, and thermal characterisation confirmed the potential of *H. sabdariffa* fibres as a reinforcing material. In view of the characterisation results, *H. sabdariffa* fibres were subsequently used to reinforce denture base acrylic resins. There were statistical differences between the denture base acrylic resins reinforced with different groups (6mm, 3mm and 300µm) of *H. sabdariffa* fibres of different weight percentages (wt%) (2.5, 5, 7.5 and 10) and the unreinforced group. The 3mm and 7.5 wt% of *H. sabdariffa* fibres produced the best improvement of the mechanical properties (FS and IS) of denture base acrylic resins (Appendix 1). Hence, the 3mm at 7.5 wt% was used in the main study, which are detailed in the following sections.

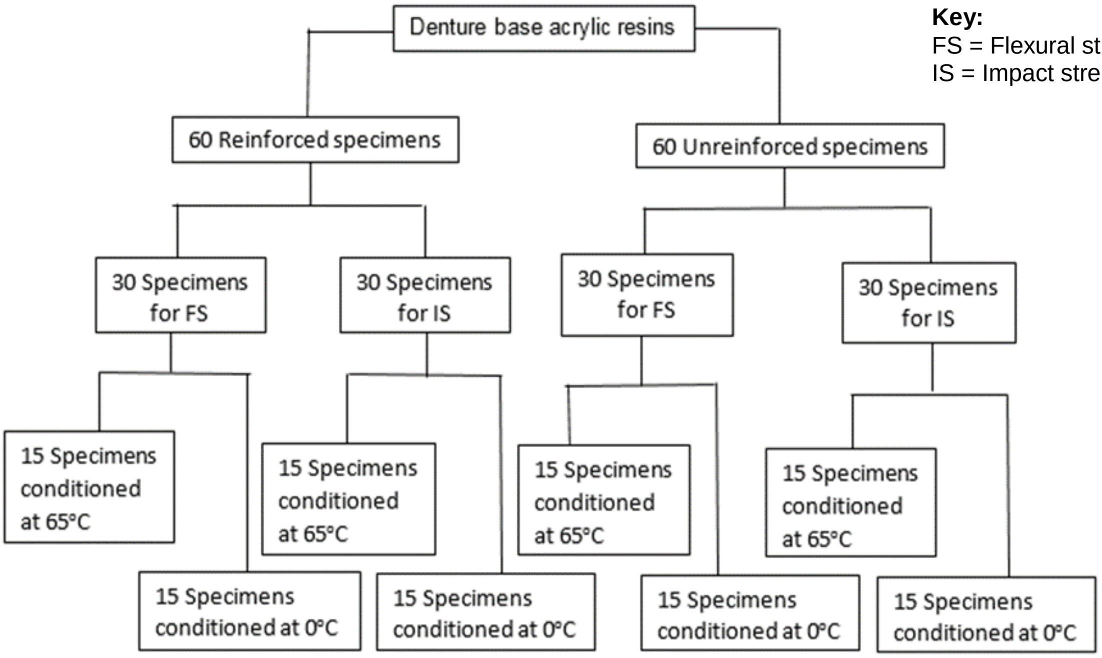
3.6 Main Study

This phase was conducted to determine the suitability of *H. sabdariffa* fibre as a reinforcing material

3.6.1 Preparation of Specimens for Flexural and Impact Strength Tests

Sample preparation followed the same procedures as outlined in Section 3.5 of this chapter. In contrast to the mixing ratio used for the fibre-reinforced specimens, the heat-cured acrylic resins mix for the unreinforced specimens was conducted according to the Vertex™ manufacturer's guidelines.

According to Somekh and Lewin (2011: 223 and 224), 30 specimens should be used in experiments where a comparison between two or more groups are made. In line with their advice, and using rectangular metal dies [Figure 3-9 (**A**)], a total of 120 specimens were prepared. Essentially, and as illustrated in Figure 3-15, there were 60 reinforced (test group) and 60 unreinforced (control group) denture base acrylic resin specimens. The two sample groups were further divided into two groups of 30 specimens each for flexural and impact testing (Figure 3-15). The reinforced sample specimens were prepared in line with the measures and procedures undertaken in Section 3.5.1 of pilot study.



Key:
FS = Flexural strength
IS = Impact strength

Figure 3-15: Overview of total sample size

The specimens for flexural and impact tests were further sub-divided into two groups. Each group (n = 15) was conditioned at 0^{o}C and 65^{o}C. This supports the argument of Senthiil and Sirsshti (2014) that temperature changes affect material behaviour intra-orally, therefore specimens must be tested at temperatures of cold liquids and hot foods. This is also consistent with Palmer, Barco and Billy (1992), and Tanaka *et al*. (1995) that extreme temperatures of foods and liquids in the mouth are within 0 C to 67^{o}C range.

3.6.2 Mechanical and Physical Testing of Specimens

From a quality and material science perspective, it is critical that all materials being tested conform to internationally accepted standards of material testing. Hence, various mechanical and physical tests were conducted (Table 3-5).

Table 3-5: Summary of test standards conducted

Mechanical and Physical Tests	Standards	Reason(s)
Flexural Strength	***ASTM D 790***	To determine resistance to repeated bending stress.
Impact Strength	***ASTM D 256***	To determine resistance to sharp and/or sudden stress.
Wear Resistance	***ASTM G 99***	To determine resistance to abrasion or surface reduction.
Hardness	***ASTM D 2583***	To determine resistance to surface scratching.
Water Absorption	***ASTM D 570***	To determine water absorption behaviour.

As described in Section 3.5.2 of pilot study, mechanical testing of the specimens was conducted. Prior to mechanical testing, and as mentioned above, all specimens were conditioned in distilled H_2O at two specified temperatures (0^oC and 65^oC) for 72 hours. It is worth noting that at the end of the 65^oC conditioning period, heat soaking of the specimens was immediately instituted by raising the temperature of the chamber to 70^oC for an hour. To maintain the temperature exposure of the specimens, all tests were carried out within 60 seconds of removing the specimens from the conditioning chambers. FS and IS testing of the specimens followed the same procedures as described in Sections 3.5.2.1 and 3.5.2.2 in pilot study, respectively.

3.6.3 Wear Resistance Test

Mathew, Shenoy and Ravishankar (2014: 71) argued that wear resistance is an effective method to understand the mechanical behaviour of dentures. A total of 20 specimens were subjected to wear resistance test. There were two sample groups (reinforced and unreinforced) of 10 specimens each. The specimens were further divided into two groups for 200g and 500g loads. Each specimen was 50mm x 10mm x 3mm (length, width and thickness respectively). As shown in Figure 3-16, and in line with the ASTM G 99 method, an in-house fabricated pin-on-disc set up machine (Mechanical Engineering Department, DUT) was used for the wear test. The tool steel disc had a surface roughness of 180µm with fixed loads of 200g and 500g [Figures 3-16(**A**) and (**B**)], respectively. The abrasive paper fixed on the steel disc polisher had a surface roughness of 180µm and a diameter 230mm. For each wear test, a new abrasive paper was used. Each specimen was subjected to a rotation speed of 300rpm for 60 seconds.

Prior to testing, each specimen was weighed (W_1). The wear test involved clamping the sample at the centre of the sample holder and the machine functioning with the fixed load for 60 seconds. The test was conducted at room temperature. Each specimen was reweighed post testing (W_2). The experiment was repeated for all samples at the 200g and 500g loads. The reason for varying the loads is to understand the effect of load on the specific wear rate. The specific wear rate of specimens was calculated using Equation 6:

$$\mathbf{K} = \Delta w / (\text{load in Newton}) \text{ x Sliding distance (gm/Nm)} \qquad \textbf{\textit{(6)}}$$

Where K = specific wear rate
Δw = change in weight
Sliding distance = 2 × π × d × rpm × t (m)
rpm of disc (300)
t = time (time each sample was exposed to grinding, in seconds)

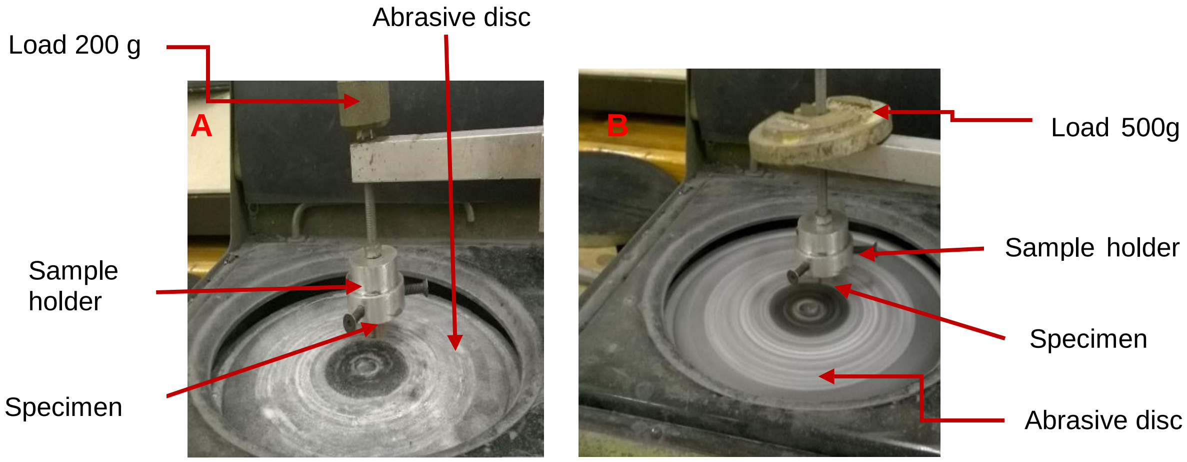


Figure 3-16: Pin-on-disc wear test
(A) Wear test with 200 grams load
(B) Wear test with 500 grams load

3.6.4 Hardness Testing

Generally, and as noted by Luyckx and Love (2004) and Hamanaka *et al*. (2016), wear resistance of materials' surface is directly proportional to the hardness. In alignment with the ASTM D 2583 standard, hardness tests were measured using a Barber Colman Barcol impressor indentation hardness test apparatus (Model GYZJ-934-1) for rigid plastics (Figure 3-17).

Figure 3-17: Barcol Impressor indentation hardness test apparatus

This indentation apparatus uses a hard steel truncated cone (indenter) at an angle of 26^0 with a flat tip of 0.157mm diameter fitted into a hollow spindle, which is held down by a spring-loaded plunger. The test specimens were placed on a flat surface with the point sleeve of the indenter positioned over it. The supporting leg was set over a specimen to counter balance the testing. A uniform downward force was incrementally applied until a maximum reading of the indenter was shown on the gauge indicator. Seventeen indentation values were captured and mean values were recorded. The hardness tests were conducted at room temperature.

3.6.5 Water Absorption Testing

Using the ASTM D 570 standard, moisture absorption of the specimens was evaluated using saturated moisture content based method, which is based on simple gravimetric principle. Two sample groups, each containing 21 specimens (10mm x 10mm x 3mm), were used for the test. The specimens were dried at 105^{o}C for 24 hours and then cooled in a desiccator to room temperature. All specimens tested were initially weighed (M_1) on a digital weighing balance (Adam® Equipment S. A. [Pty]

Johannesburg, South Africa) with an accuracy of 0.001g in dry conditions. Water absorption tests were carried as follows:

- The specimens were immersed in de-ionised water in a beaker at room temperature.
- After a 24 hour immersion period, specimens were removed from the beaker.
- All surface water was gently dried using an absorbent paper towel, and the specimens immediately reweighed within 60 seconds.
- The specimens were returned to the de-ionised water and subsequently weighed at intervals of 2 hours until they reached saturation limits, that is, when no weight differences were measured (M_2).
- Finally, and using Equation 7, the moisture absorption rate was determined as the weight gained per volume of specimen and average values reported.

$$\textbf{Moisture absorption} = \frac{M_2 - M_1}{\text{Volume of specimen}} \quad \text{in (mg/cm}^3\text{)} \qquad \textbf{(7)}$$

3.6.6 Microstructural Analysis of the Specimens

A FE-SEM (Ultra Series®, Carl Zeiss, GmbH) analysis was conducted to characterise the microstructure of the bond between the matrix and *H. sabdariffa* fibres of the reinforced and unreinforced sample groups. Prior to the FE-SEM analysis, the surfaces of the samples were sputtered with a thin layer of gold to ensure good conductivity of the materials and to prevent accumulation of electrostatic charge. The FE-SEM operated at 20 KV under controlled atmospheric conditions.

3.7 Analysis of Data

The analysis of data was accomplished using descriptive and inferential statistics. According to Argyrous (2013), descriptive statistics are numerical, graphical and tabular techniques for organising, analysing and presenting data obtained from the various experiments. In addition, descriptive statistics neither infer nor predict an outcome of such data; instead, they summarise the results of experiments. Inferential statistics, by contrast, is the numerical statistical technique for reaching conclusions about a sample data, and is a system of testing hypothesis by “examining the relationship among variables” (Creswell 2014).

In testing the hypothesis as outlined in Section 1.7, independent t-test was used to analyse and compare the mean differences between the reinforced and the unreinforced denture base acrylic resins. The level of significance was $p < 0.05$. A critical point to note is that where results were not normally distributed, a Mann-Whitney test was used to analyse and compare the mean differences between the reinforced and the unreinforced denture base acrylic resins. This was in line with the advice provided by Field (2000) and Barnes (2011). All data were analysed using SPSS (Version 23®).

3.8 Validity and Reliability

Roberts, Priest and Traynor (2006) emphasised that the effectiveness of any research depends on its ability not to mislead its users. They described the validity of quantitative research design and experimental research strategy as being related to the credibility of the research, and is based on features such as the tools, methods and procedures of data collection, analysis, and conclusions drawn. Consequently, criterion validity premised on internal validity was used to ensure accurate analysis of data. As highlighted by Leedy and Ormrod (2005), internal validity allows precise conclusions about cause and effect relationships within data. Therefore, testing of specimens followed ISO 1567: 1999, together with the various standards as shown in Table 3-5. Furthermore, all equipment were properly calibrated prior to testing and analysis of specimens (Appendices 2 and 3).

Reliability of experimental research, and as explained by Izedonmi (2005: 128) and Roberts *et al*. (2006: 42), is the degree to which experimental procedures are reproducible and repeatable in different settings. Repeatability of tests were confirmed in terms of the specimens within the study showing similar values.

Overall, this chapter has detailed the research paradigm and experimental procedures adopted in this study. The subsequent chapters explain the results and provide an in-depth discussion of the main study, while highlighting the recommendations and directions for future research.

Chapter 4 – Results and Discussion

This chapter presents the results and discussion of the main study of the research. The aim of the study was to determine the suitability of *H. sabdariffa* fibres as reinforcing material for denture base acrylic resins is subsequently explained. The data collected was analysed in relation to the research objectives in Section 1.6. This entailed evaluating the FS and IS of both reinforced and unreinforced denture base acrylic resins at different conditioning temperatures in line with ASTM D 790 and D 256. Similarly, and using ASTM G 99, D 2583 and D 570, the wear resistance, hardness and moisture absorption behaviour of the reinforced and unreinforced denture base acrylic resins was also examined. Microstructural characterisation was further investigated in order to show the extent of bonding between denture base acrylic resins and the *H. sabdariffa* fibres. This chapter concludes with a summary of the various data analysed. For the purpose of strengthening the arguments presented within this chapter, Figure 4-1 clarifies the differences between composite, polymer matrix and *H. sabdariffa* reinforcing fibres. The matrix is the primary material (denture base acrylic resin) into which the reinforcing fibres (*H. sabdariffa*) are intimately embedded. This interaction between the two materials enables the transfer of stress from matrix to reinforcing material. While the matrix provides the body of material, the reinforcing fibres improves strength by bearing the loads/forces applied.

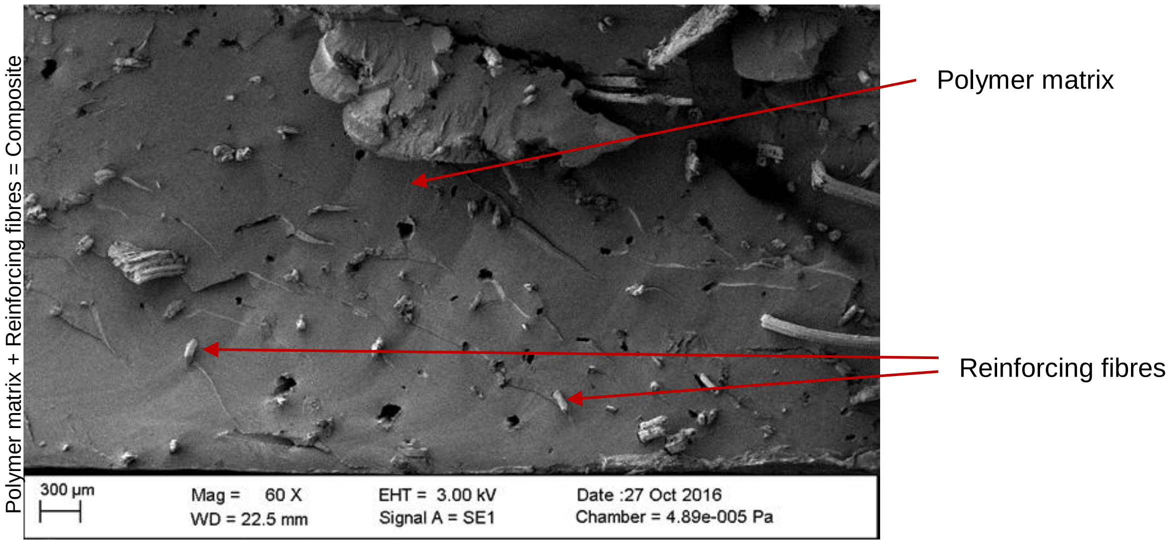


Figure 4-1: Polymer matrix-reinforcing fibres interaction in composite

4.1 The Suitability of *Hibiscus sabdariffa* Fibre as a Reinforcing Material

4.1.1 Flexural and Impact Strength

The results in Table 4-1 highlight the FS between the reinforced and unreinforced sample groups effect of different temperatures. Significant differences were found in the FS of *H.* sabdariffa fibre-reinforced and unreinforced denture base acrylic resins at 0°C ($p < 0.000$) and 65°C ($p < 0.025$). From Figure 4-2, *H. sabdariffa* fibre-reinforced denture base acrylic resins had the highest mean values that is 87.80 MPa (± 8.20) at 0°C and 75.19 MPa (± 9.38) at 65°C. These results demonstrate that FS of *H. sabdariffa* fibre-reinforced denture base acrylic resins increased by 18% and 11% at 0°C and 65°C, respectively.

Table 4-1: Effect of reinforcement (flexural strength) at different conditioning temperature

Sample groups (°C)	**Descriptive and Inferential statistics**		
	n	**Mean ± SD**	**t- test ($p < 0.05$)**
Unreinforced **(0 °C)**	15	74.34 ± 9.73	0.000
Reinforced **(0 °C)**	15	87.80 ± 8.20	
Unreinforced **(65 °C)**	15	67.48 ± 8.40	0.025
Reinforced **(65°C)**	15	75.19 ± 9.38	

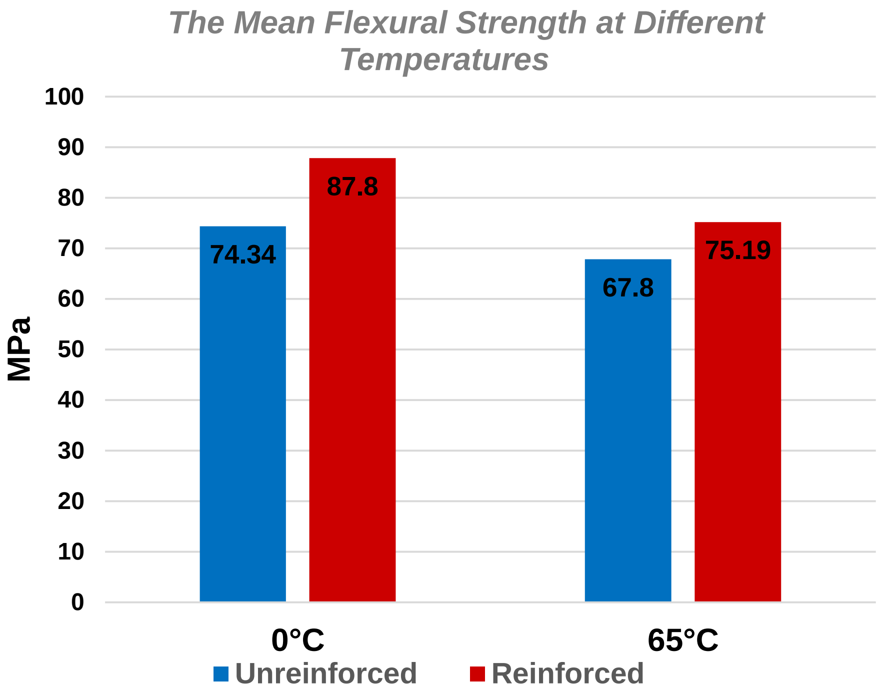


Figure 4-2: The mean flexural strength of denture base acrylic resins at different temperatures

Similarly, the results in Table 4-2 show the IS of the two sample groups at different temperatures. In contrast to the unreinforced denture base acrylic resins, the IS of the *H. sabdariffa* fibre-reinforced denture base acrylic resins at 0°C ($p < 0.031$) and at 65°C ($p < 0.0001$) were significantly different. Figure 4-3, further highlights that *H. sabdariffa* fibre-reinforced denture base acrylic resins was more than twice the strength of the unreinforced denture base acrylic resins at 65°C.

Table 4-2: Effect of reinforcement (impact strength) at different conditioning temperatures

Sample groups (°C)	Descriptive and Inferential statistics		
	n	Mean ± SD	t-test ($P < 0.05$)
Unreinforced **(0 °C)**	15	12.42 ± 0.002836109	0.031
Reinforced **(0 °C)**	15	17.23 ± 0.007699962	
Unreinforced **(65 °C)**	15	9.04 ± 0.003237413	0.000
Reinforced **(65 °C)**	15	22.60 ± 0.012900964	

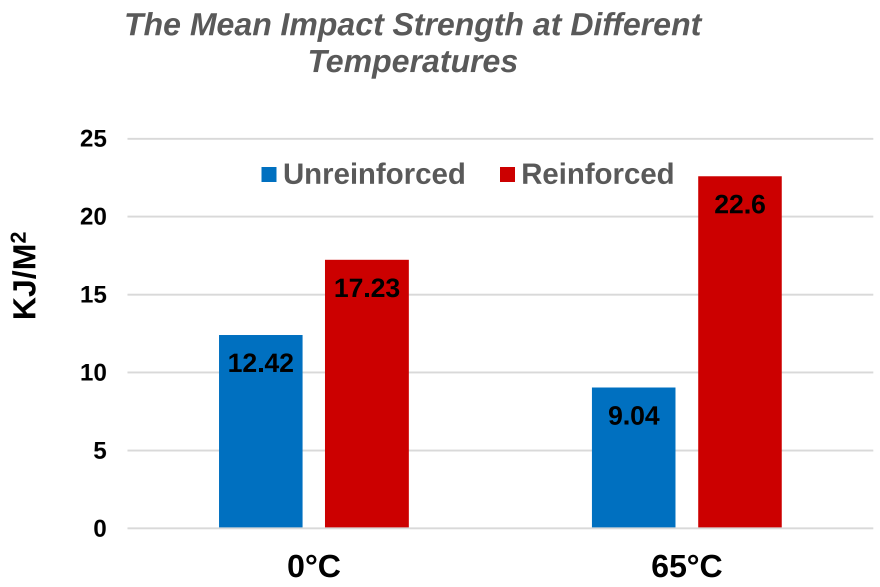


Figure 4-3: The mean impact strength of denture base acrylic resins at different temparatures

In light of the aforementioned results, the alternate hypothesis *(H_1)* that is *H. sabdariffa* fibres improve flexural and impact strengths of denture base acrylic resins was therefore accepted. Several authors (Karacaer *et al*. 2003; Singha and Thakur 2008b; Geerts *et al.* 2008; Bashi and Al-Nema 2009; Iqbal and Naqash 2014; Murthy *et al*. 2015) have elaborated that the mechanical properties of fibre-reinforced composite is enhanced by the ability of the matrices to transfer load to the reinforcing fibres. This is primarily facilitated by the interfacial bonding between the fibres and the matrices. These authors however, did not take cognisance of the effect of different conditioning temperatures on the mechanical properties of denture base acrylic resins, which was a focus in this study. Consumed foods and liquids have different extreme temperatures and therefore may have different effects on materials intra-orally. It is therefore important to consider the effects these extreme temperatures may have on the FS and IS of denture base acrylic resins. Moreover, the increased results in FS and IS support Thomas and Pothan (2008) finding that fibre modification through mercerisation alters the topography of lignocellulosic fibres such as *H. sabdariffa* in the reinforcement of polymers, as it roughens the fibres and acivates the OH goups. This causes an interlocking reaction between the fibres and polymer matrices, thereby enabling the load to be transferred to the reinforcing fibres.

Furthermore, from the results, it can be assumed that increased surface area promotes effective adhesion between the reinforcing fibres and the denture base acrylic resins. This is consistent with several studies (Ashori 2008; Ashori and Nourbakhsh 2010; Rezvani, Atai and Hamze 2013; Arsene *et al*. 2013; Shouha, Swain and Ellakwa 2014). From a dental laboratory perspective, this study further corroborates the findings of Ladha and Shah (2011) and Murthy *et al*. (2015) that pre-impregnating *H. sabdariffa* fibres with monomer prior to mixing can have a positive impact on the overall FS and IS of the denture base acrylice resins.

In reviewing the literature (Vojvodic *et al*. 2008; Shehata, Mostafa and Moubarak 2015), it can be seen that the process of conditioning denture base acrylic resins at elevated temperatures post the curing cycle causes a reduction in residual monomer. As argued by Vojvodic *et al.* (2008), residual monomer acts as a plasticiser, thereby reducing the strength properties of the composite. It can therefore be ascertained that the IS of *H. sabdariffa* fibre-reinforced denture base acrylic resins is more likely to increase at 65^{o}C. Notwithstanding this, molecular movement of polymer chains increase as the conditioning temperature increases thereby lowering the resistance of denture base acrylic resins to fracture. This could have accounted for the reduced FS of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins sample groups at 65^{o}C. These results confirm Oku’s (1989) argument that a decrease in strength properties of denture base acrylic resins is caused by elevated conditioning temperatures. Additionally, the thermally stable mercerised *H. sabdariffa* fibres within the denture base acrylic resins mass restricts molecular movement between the polymer chains. Essentially, this improves the mechanical properties of *H. sabdariffa* fibre-reinforced denture base acrylic resins, overall.

4.1.2 Wear Resistance

As presented in Table 4-3 and illustrated in Figure 4-4 there were significant differences in the specific wear rates of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins at 500g load test ($p < 0.044$). In particular, the wear rate of the *H. sabdariffa* fibre-reinforced sample group was 9.23 x 10^{-7} g/NM (± .0000000792), while the unreinforced sample group was 2.676 x 10^{-6} g/NM (±. 0000001440). In contrast, there were no significant differences ($p > 0.156$) in the specific wear rates at the 200g load test between the two sample groups. Regardless of this, and a point which deserves mentioning, is that the *H. sabdariffa* fibre-reinforced denture base acrylic resin specimens had a lower wear rate than the unreinforced denture base acrylic resin specimens that is 4.762 x 10^{-7} g/NM.

Table 4-3: Specific wear rate of sample groups at 500g and 200g loads

Sample Groups (g)	**Descriptive and Inferential Statistics**			
	n	**Mean** g/NM	**SD**	**t-test (p<0.05)**
Unreinforced **(500 g)**	5	2.676 x 10^{-6}	.0000001440	0.044
Reinforced **(500 g)**	5	9.23 x 10^{-7}	.0000000792	
Unreinforced **(200 g)**	5	1.7392 x 10^{-6}	.0000017545	0.156
Reinforced **(200 g)**	5	4.762 x 10^{-7}	.000004274	

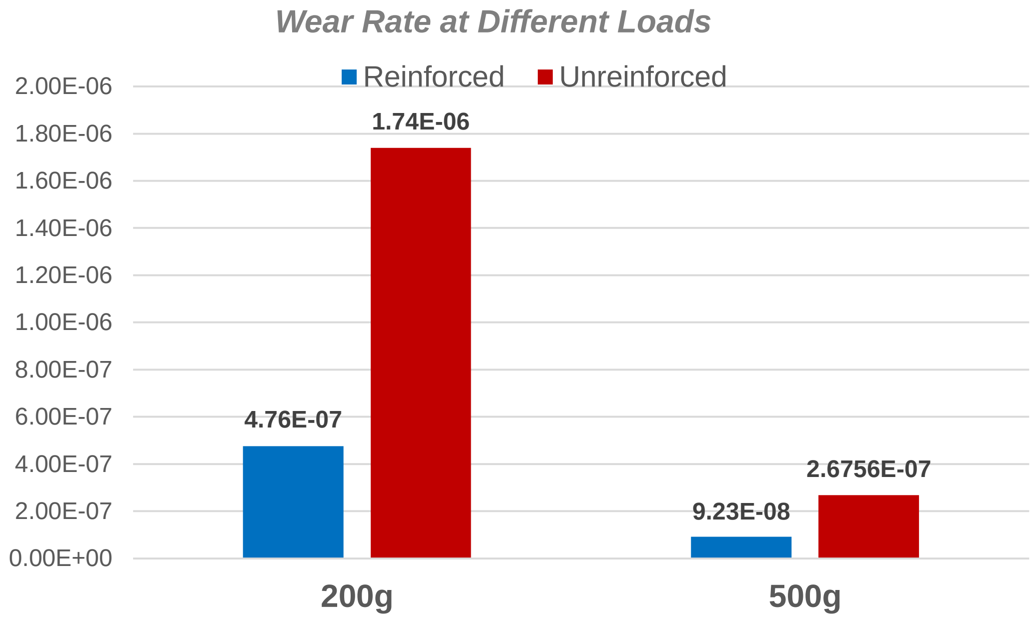


Figure 4-4: The mean specific wear rate of denture base acrylic resins at 200g and 500 loads

The increased wear resistance of the *H. sabdariffa* fibre-reinforced sample group could possibly be explained by the improvement in the mechanical properties, that is, the intimate adhesion between the mercerised *H. sabdariffa* fibres and denture base acrylic resins. The compact and smooth microstructure of the reinforced denture base acrylic resin in Figure 4-7(**B**) further supports the intimate adhesion. This corroborates with the work of several authors (Gurbuz *et al.* 2005; Singha and Thakur 2008a; Hahnel *et al*. 2009; Shetty and Shenoy 2010; Rokbi *et al*. 2011; Benyahia *et al*. 2013; Isa *et al*. 2014; Mathew, Shenoy and Ravishankar 2014; Ismaeel *et al*. 2015), that composites reinforced with mercerised fibres are compact thereby improving wear resistance. In contrast, and as illustrated in Figure 4-7(**A**), the microstructure of the unreinforced denture base acrylic resin was non-compact and rough. Clinically, and in agreement with Suwannaroop *et al*. (2011) and Mathew, Shenoy and Ravishankar (2014), the above results are valuable as they suggest that denture wear rate intra-orally is likely to decrease.

4.1.3 Hardness

Table 4-4 and Figure 4-5 present the hardness results of the reinforced and unreinforced denture base acrylic resins. Unlike other studies (Farina *et al*. 2012; Ahmed and Ebrahim 2014; Ismaeel *et al*. 2015), which showed that reinforcement significantly improves the hardness of composites, there was no significant differences (*p* > 0.707) between the unreinforced and reinforced denture base acrylic resins. In support of Fatihallah's (2015) and Jassim's (2015) argument, a factor contributing to the results not being significantly different could have been that the *H. sabdariffa* fibres were within the denture base acrylic resin and not near the surface of the composite. From a clinical point of view, it can further be inferred that *H. sabdariffa* fibre-reinforced acrylic resins are not highly rigid and will therefore not compromise their functional efficiency intra-orally. This means that the denture will not traumatise the oral soft tissues during use. This aligns with the recent work of Ibrahim (2015) and Duymus *et al*. (2016). Arising from the aforementioned results, the alternate hypothesis *(H_1)* that is *H. sabdariffa* fibres improves the wear resistance and hardness properties of denture base acrylic resins was therefore accepted.

Table 4-4: Barcol hardness of sample groups

Sample groups	**Descriptive and Inferential statistics**		
	n	**Mean ± SD**	**t-test (*p* < 0.05)**
Unreinforced group	17	37.18 ± 3.17	0.707
Reinforced group	17	37.59 ± 3.16	

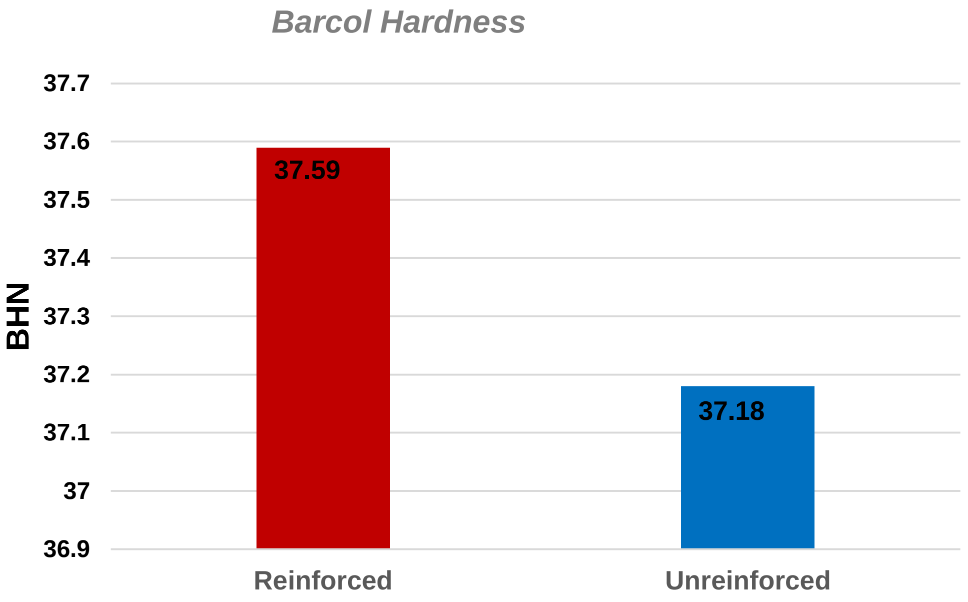


Figure 4-5: Mean Barcol hardness results of denture base acrylic resins

4.1.4 Water Absorption Behaviour

Table 4-5 and Figure 4-6 present the water absorption behaviour of *H. sabdariffa* fibre-reinforced and unreinforced denture base acrylic resins. The Shapiro-Wilk test used revealed that the results were not normally distributed ($p < 0.000$); the Mann-Whitney non-parametric test was therefore used. Significant differences ($p < 0.041$) in the water absorption rates between the *H. sabdariffa* fibre-reinforced and the unreinforced denture base acrylic resins were revealed. The increase in water absorption rate could have been caused by the lignocellulosic nature of the fibres, which increasingly absorbs and retains water molecules within the composite. This can be confirmed by the assertions made by several other authors (Vilay *et al*. 2008; Alomayri *et al*. 2014; Banga, Singh and Choudhary 2015) that natural fibres have a high water absorption rate. Concomitantly, the porous nature of denture base acrylic resins also enables absorption of water. This is in agreement with several studies (Ayad, Badawi and Fatah 2008; Tuna *et al.* 2008; Durkan *et al*. 2010; Asopa *et al*. 2015) that reinforcement increases the water absorption behaviour of denture base acrylic resins.

Table 4-5: Water absorption behaviour of sample groups

Sample groups	Descriptive and Inferential statistics			
	n	Mean ± SD	Mann-Whitney test	Level of Significance ($p < 0.05$)
Unreinforced group	21	0.1900 ± 0.175	140.500	0.041
Reinforced group	21	0.2200 ± 0.1273		

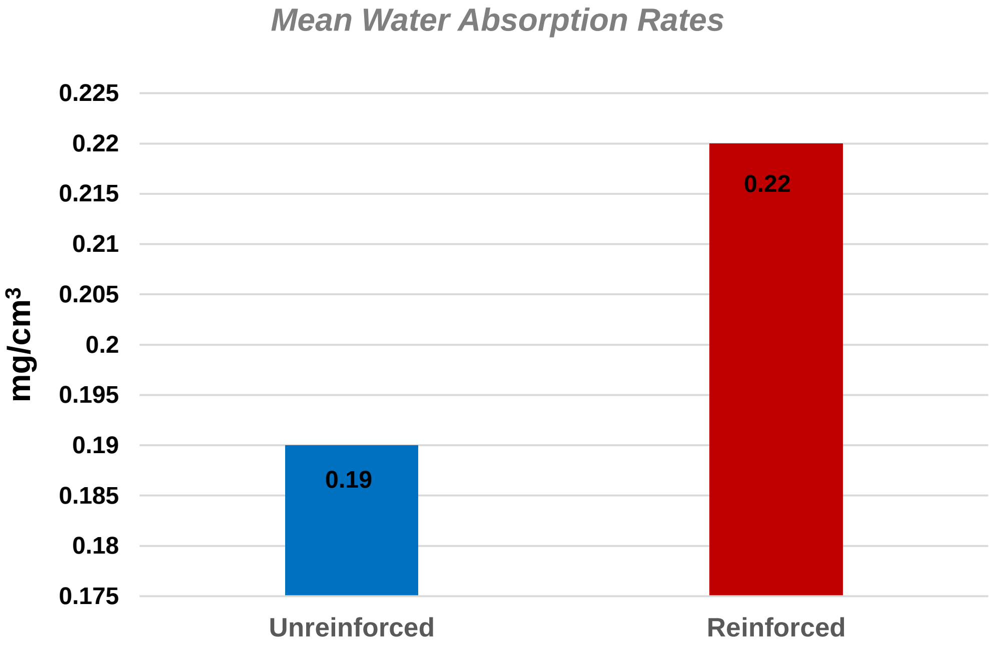
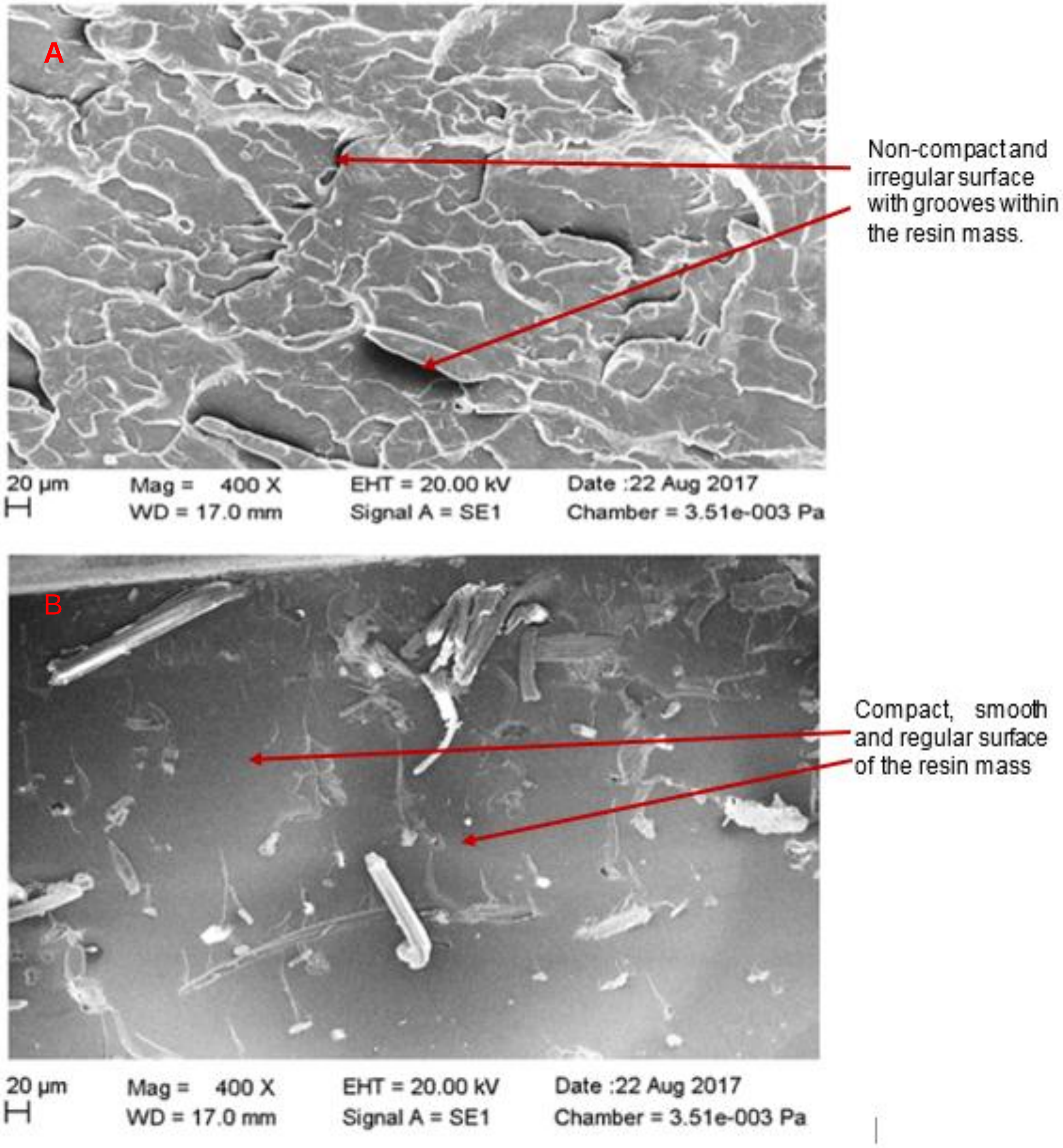


Figure 4-6: Mean water absorption rates of denture base acrylic resins

From the aforementioned water absorption results, it can further be contended that fibre treatment through mercerisation reduces hemicellulose content of *H. sabdariffa* fibres and limits the uptake of water thereby enhancing interfacial bond between the *H. sabdariffa* fibres and denture base acrylic resins. This can be supported by the arguments of Tham, Chow and Ishak (2010), Sampathkumar *et al*. (2012), and Ichetaonye *et al*. (2015) that mercerisation imparts barrier properties to lignocellulosic fibres. From a denture base acrylic resins perspective, Craig (1993), McCabe and Walls (2009), and Bonsor and Pearson (2013) argued that even though water absorption causes acrylic resins to expand, this expansion compensates for polymerisation shrinkage, hence the material remains dimensionally stable. In view of the above results, the null hypothesis *(H_o)* that is *H. sabdariffa* fiber does not improve resistance to water absorption by denture base acrylic resins was therefore accepted. Despite the increase in water absorption of *H. sabdariffa* fibre-reinforced denture base acrylic resins, the rate is within the ISO 1567: 1999 (ANSI/ADA) specification No. 12: 2002 limit.

4.1.5 Microstructural Analysis

As mentioned earlier in this chapter, the unreinforced denture base acrylic resin specimens in Figure 4-7(**A**) show a non-compact and irregular microstructure with grooves internally. The *H. sabdariffa* fibre-reinforced denture base acrylic resins [Figure 4-7(**B**)], by contrast, have a smooth, compact and organised microstructure. These microstructural differences could be attributed to the rough surfaces of the mercerised *H. sabdariffa* fibres which enabled the denture base acrylic resins to penetrate into the fibres. This confirms the findings made by several authors (Vilay *et al.* 2008; Jayabal *et al*. 2012; Chandramohan and Bharanichandar 2013; Abral *et al*. 2013; Alomayri *et al*. 2014 and Fonseca *et al*. 2014) that mercerisation improves fibre-polymer bonding, thereby improving the mechanical properties of composites. A critical point worth mentioning is that there were no pulling out of fibres from the matrix within the composite. Fibre pull-out is a phenomenon of separation of fibre from matrix due to insufficient adhesion between the fibre and the matrix within a composite. Authors such as Dassios (2007) and Vilay *et al*. (2008) have contended that fibre pull-out effectively reduces the mechanical properties of the composite. Hence, the results of this study reaffirm the importance of fibre treatment.



Non-compact and irregular surface with grooves within the resin mass.

Compact, smooth and regular surface of the resin mass

Figure 4-7: FE-SEM images of fractured denture base acrylic resins: (A) unreinforced; (B) reinforced

Compliance to the conditions set out in ISO 1567, ASTM D 256, D 790, G 99, D 2583 and D 570 in preparing and testing of the specimens, as well as calibration of the equipment and instruments underpin the validity of the results of this study. Similarly, the repeatability of tests in terms of number of specimens and similarity in the results obtained from the various tests underpin the reliability of the results of this study.

Overall, the prominent features of this study showed that mercerised *H. sabdariffa* fibres at various conditioning temperatures significantly improved the mechanical properties of denture base acrylic resins. Importantly, the FE-SEM images of the *H. sabdariffa* fibre-reinforced acrylic denture base resins confirmed that there were no fibre pull-outs, so it ultimately did not compromise FS and IS. Considering the results of this study, align with the availability, renewability, low cost, environmental friendliness, and easy to use equipment in the production and utilisation of *H. sabdariffa* fibres, these fibres are therefore considered a suitable reinforcement material for denture base acrylic resins. Moreover, mechanical and physical properties of the *H. sabdariffa* fibres reinforced denture base acrylic resins complied with ISO 1567 for all denture base materials. The next chapter provides the conclusions drawn from the study, identifies limitations and recommends future directions for research.

Chapter 5 – Conclusion and Recommendations

This study examined the suitability of *H. sabdariffa* fibres as a reinforcing material for denture base acrylic resins. A positivist research paradigm and experimental design approach was followed. The preliminary phase of the study focused on the physical, chemical and thermal characterisation of *H. sabdariffa* fibres. The pilot study evaluated the reinforcing ability of *H. sabdariffa* fibres. The main study evaluated the suitability of *H. sabdariffa* fibres as a reinforcement material for denture base acrylic resins. This involved examining the FS and IS of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins at different conditioning temperatures. In addition, wear resistance, hardness and water absorption behaviour of the two sample groups were investigated. Drawing from the discussions of the aforementioned phases, this chapter makes recommendations on fibre length and fibre weight percentage (wt%) to be used in dental laboratory practice and concludes by proposing future directions for research.

5.1 Conclusion

The salient results of this study revealed that mercerisation improves thermal stability of *H. sabdariffa* fibres, as well as the interfacial bonding between the fibres and denture base acrylic resins thereby improving the mechanical properties. From a dental laboratory based practice point of view, the 3mm fibre length and the 7.5 wt% of *H. sabdariffa* fibre provides a useful guide in reinforcing denture base acrylic resins. The FS and IS achieved were in line with ISO 1567 that is the strength results were not below 65MPa. Hence, it can be concluded that *H. sabdariffa* fibre is a suitable reinforcement material for denture base acrylic resins.

5.2 Recommendations

Given the limited research into the effect of different conditioning temperatures on the mechanical properties of denture base acrylic resins, further research is needed to understand how temperature affects the FS and IS of reinforced denture base acrylic resins in relation to intra-oral use. A limitation that emerged through the results of this study was the high water absorption rate caused by the lignocellulosic nature of *H. sabdariffa* fibres. Other fibre treatment processes need to be explored to improve the barrier properties of *H. sabdariffa* fibres and is therefore an area of further research. From a quality control perspective, dental manufacturers can be guided by the results of this study on the volume of fibres to use in polymer production.

Furthermore, a significant implication of using *H. sabdariffa* fibres as a reinforcement material is to examine the synthesis of nano-cellulose extracts of natural fibres and nano-metallic materials to improve the mechanical properties of denture base acrylic resins. This unchartered research area could lead to a nuanced understanding of nano-metallic materials that have microbial inhibition potential intra-orally. For clinical situations, any further research using *H. sabdariffa* fibre need to include in vitro and in vivo investigations.

In view that the monomer ratio was increased to pre-impregnate natural fibers to sufficiently to bond within the matrix, another area of work to be considered is the powder liquid ratio influence on the flexural and impact strengths of *H. sabdariffa* fibre reinforced acrylic resins.

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Appendices

Appendix 1 – Results of Pilot Study

Table 1: Statistical analysis of the flexural properties of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins

Sample groups	n	Mean ± SD	Std Error	95% Confidence Interval for Mean		ANOVA test (p-value)
				Lower Bound	Upper Bound	
Unreinforced	5	83.55 ±.61818	.27646	82.7806	84.3158	0.001
Reinforced 6 mm 2.5 wt%	5	92.64 ± 7.29814	3.26382	83.5774	101.7010	
Reinforced 6 mm 5.0 wt%	5	84.11 ± 4.51764	2.02035	78.4960	89.7148	
Reinforced 6 mm 7.5 wt%	5	87.88 ± 4.30209	1.92395	82.5342	93.2178	
Reinforced 6 mm 10 wt%	5	81.75 ± 3.47382	1.55354	77.4357	86.0623	
Reinforced 3 mm 2.5 wt%	5	68.84 ± 4.29366	1.92018	63.5107	74.1733	
Reinforced 3 mm 5.0 wt%	5	75.58 ± 3.67622	1.64406	71.0174	80.1466	
Reinforced 3 mm 7.5 wt%	5	101.20 ± 3.63543	1.62581	96.6844	105.7124	
Reinforced 3 mm 10 wt%	5	88.67 ± 13.75215	6.15015	71.5905	105.7415	
Reinforced 300 µm 2.5 wt%	5	93.80 ± 8.48953	3.79663	82.5039	103.5861	
Reinforced 300 µm 5.0 wt%	5	88.97 ± 5.73351	2.56411	81.8503	96.0885	
Reinforced 300 µm 7.5 wt%	5	87.20 ± 3.53609	1.58139	82.8064	91.5876	
Reinforced 300 µm 10 wt%	5	79.87 ± 1.10755	.49531	78.4978	81.2482	
Total	65	85.6377 ± 9.59366	1.18995	83.2605	88.0149	

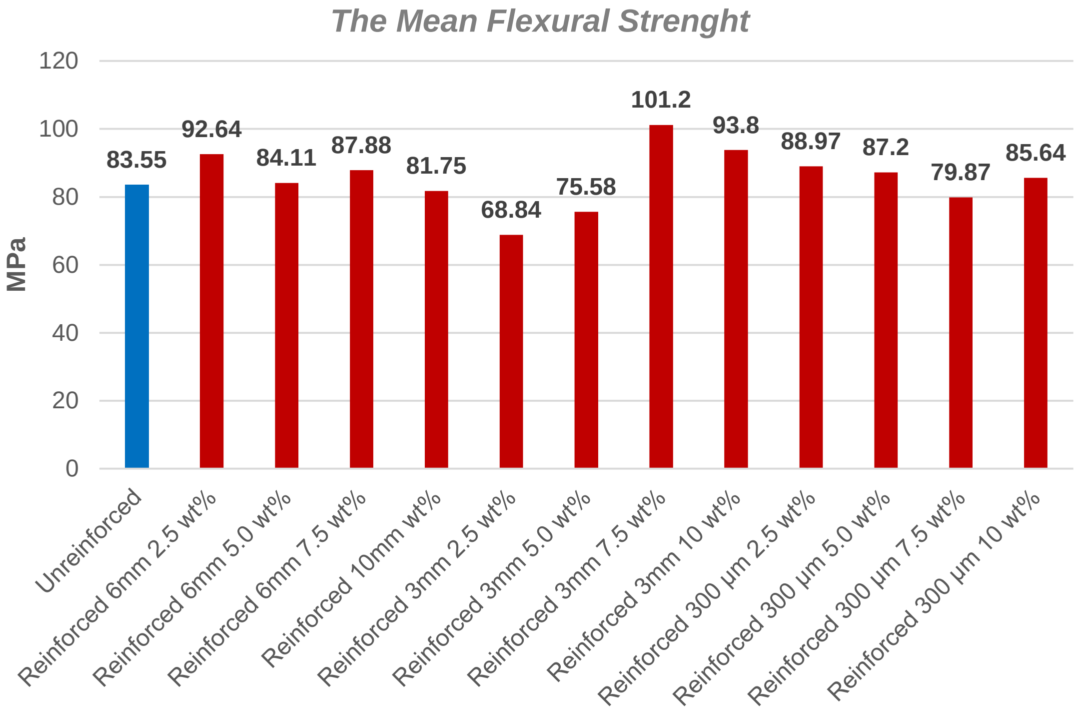


Figure 1: Mean flexural strength of the sample groups

From Table 1 and Figure 1, there were significant differences ($p < 0.001$) in the flexural strength of denture base acrylic resins reinforced with *H. sabdariffa* fibres of different sizes (6 mm, 3 mm and 300 µm) and wt% (2.5, 5.0, 7.5, 10). The denture base acrylic resins reinforced with 3 mm *H. sabdariffa* fibre at 7.5 wt% had the highest mean (101.20 ± 3.64 MPa), while the PMMA specimens reinforced with *H. sabdariffa* fibre 300 µm at 10 wt% loading had the lowest mean (79.87 ± 1.12 MPa). Denture base acrylic resins reinforced with 3mm *H. sabdariffa* fibre at 7.5 wt% loading was therefore selected for the main study.

Table 2: Bonferroni test for flexural properties of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins

Groups comparison	P-value	Significance
Unreinforced - Reinforced 6 mm 2.5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 7.5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 10 %	1.000	Non-significant
Unreinforced - Reinforced 3 mm 2.5 %	0.020	Significant
Unreinforced - Reinforced 3 mm 5 %	1.000	Non-significant
Unreinforced - Reinforced 3 mm 7.5 %	0.001	Significant
Unreinforced - Reinforced 3 mm 10 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 2.5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 7.5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 6 mm 5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 6 mm 7.5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 6 mm 10 %	0.423	Non-significant
Reinforced 6mm 2.5% - Reinforced 3 mm 2.5 %	0.000	Significant
Reinforced 6mm 2.5% - Reinforced 3 mm 5 %	0.003	Significant
Reinforced 6mm 2.5% - Reinforced 3 mm 7.5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6mm 2.5% - Reinforced 300 µm 10 %	0.101	Non-significant
Reinforced 6mm 5% - Reinforced 6 mm 2.5 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 6 mm 7.5 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 6 mm 10 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 3 mm 2.5 %	0.013	Significant
Reinforced 6mm 5% - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 3 mm 7.5 %	0.002	Significant
Reinforced 6mm 5% - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 300 µm 5 %	1.000	Non-significant

Reinforced 6mm 5% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6mm 5% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 6 mm 10 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 3 mm 2.5 %	0.000	Significant
Reinforced 6mm 7.5% - Reinforced 3 mm 5 %	0.146	Non-significant
Reinforced 6mm 7.5% - Reinforced 3 mm 7.5 %	0.064	Non-significant
Reinforced 6mm 7.5% - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6mm 7.5% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6mm 10% - Reinforced 3 mm 2.5 %	0.090	Non-significant
Reinforced 6mm 10% - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6mm 10% - Reinforced 3 mm 7.5 %	0.000	Significant
Reinforced 6mm 10% - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6mm 10% - Reinforced 300 µm 2.5 %	0.310	Non-significant
Reinforced 6mm 10% - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6mm 10% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6mm 10% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3mm 2.5% - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 3mm 2.5% - Reinforced 3 mm 7.5 %	0.000	Significant
Reinforced 3mm 2.5% - Reinforced 3 mm 10 %	0.000	Significant
Reinforced 3mm 2.5% - Reinforced 300 µm 2.5 %	0.000	Significant
Reinforced 3mm 2.5% - Reinforced 300 µm 5 %	0.000	Significant
Reinforced 3mm 2.5% - Reinforced 300 µm 7.5 %	0.001	Significant
Reinforced 3mm 2.5% - Reinforced 300 µm 10 %	0.381	Non-significant
Reinforced 3mm 5% - Reinforced 3 mm 7.5 %	0.000	Significant
Reinforced 3mm 5% - Reinforced 3 mm 10 %	0.078	Non-significant
Reinforced 3mm 5% - Reinforced 300 µm 2.5 %	0.002	Significant
Reinforced 3mm 5% - Reinforced 300 µm 5 %	0.061	Non-significant
Reinforced 3mm 5% - Reinforced 300 µm 7.5 %	0.247	Non-significant
Reinforced 3mm 5% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3mm 7.5% - Reinforced 3 mm 10 %	0.121	Non-significant
Reinforced 3mm 7.5% - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 3mm 7.5% - Reinforced 300 µm 5 %	0.154	Non-significant
Reinforced 3mm 7.5% - Reinforced 300 µm 7.5 %	0.037	Significant

Reinforced 3mm 7.5% - Reinforced 300 µm 10 %	0.000	Significant
Reinforced 3mm 10% - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 3mm 10% - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 3mm 10% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 3mm 10% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 300µm 2.5% - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 300µm 2.5% - Reinforced 300 µm 7.5%	1.000	Non-significant
Reinforced 300µm 2.5% - Reinforced 300 µm 10%	0.073	Non-significant
Reinforced 300µm 5% - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 300µm 5% - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 300µm 7.5% - Reinforced 300 µm 10%	1.000	Non-significant

As illustrated in Table 3 and Figure 2, significant differences ($p < 0.013$) were revealed in the impact strength of *H. sabdariffa* fibre-reinforced denture base acrylic resins of different sizes (6 mm, 3 mm and 300 µm) and wt% (2.5, 5.0, 7.5, 10). Overall, the specimens reinforced with 3mm *H. sabdariffa* fibres at 7.5 wt% had the highest mean (32.01 ± 0.0153 KJ/M^2), while the specimens reinforced with 6mm *H. sabdariffa* fibres at 5 wt% had the lowest mean (13.18 ± 0.0017 KJ/M^2). Denture base acrylic resins reinforced with 3mm *H. sabdariffa* fibre at 7.5 wt% was therefore selected the main study.

Table 3: Statistical analysis of impact properties of unreinforced and *H. sabdariffa* fibre-reinforced specimens

Sample groups	**n**	**Mean ± SD**	**Std Error**	**95% Confidence Interval of Mean**		**ANOVA test *(P-value)***
				Lower Bound	**Upper Bound**	
Unreinforced	5	14.12 ±.00346	.00155	.0098	.0184	0.013
Reinforced 6 mm 2.5 wt%	5	15.05 ±.00352	.00157	.0107	.0194	
Reinforced 6 mm 5.0 wt%	5	13.18 ±.00176	.00079	.0110	.0154	
Reinforced 6 mm 7.5 wt%	5	19.77 ±.00932	.00417	.0082	.0313	
Reinforced 6 mm 10 wt%	5	23.53 ±.00312	.00140	.0197	.0274	
Reinforced 3 mm 2.5 wt%	5	17.89 ±.00695	.00311	.0093	.0265	
Reinforced 3 mm 5 wt%	5	23.53 ±.00640	.00286	.0156	.0315	
Reinforced 3 mm 7.5 wt%	5	32.01 ±.01536	.00687	.0129	.0511	
Reinforced 3 mm 10 wt%	5	24.48 ±.01022	.00457	.0118	.0372	
Reinforced 300 µm 2.5 wt%	5	22.03 ±.00542	.00242	.0153	.0288	
Reinforced 300 µm 5.0 wt%	5	28.24 ±.01560	.00698	.0089	.0476	
Reinforced 300 µm 7.5 wt%	5	29.18 ±.01110	.00496	.0154	.0430	
Reinforced 300 µm 10 wt%	5	29.18 ±.00834	.00373	.0188	.0395	
Total	65	22.50 ±.00998	.00124	.0200	.0250	

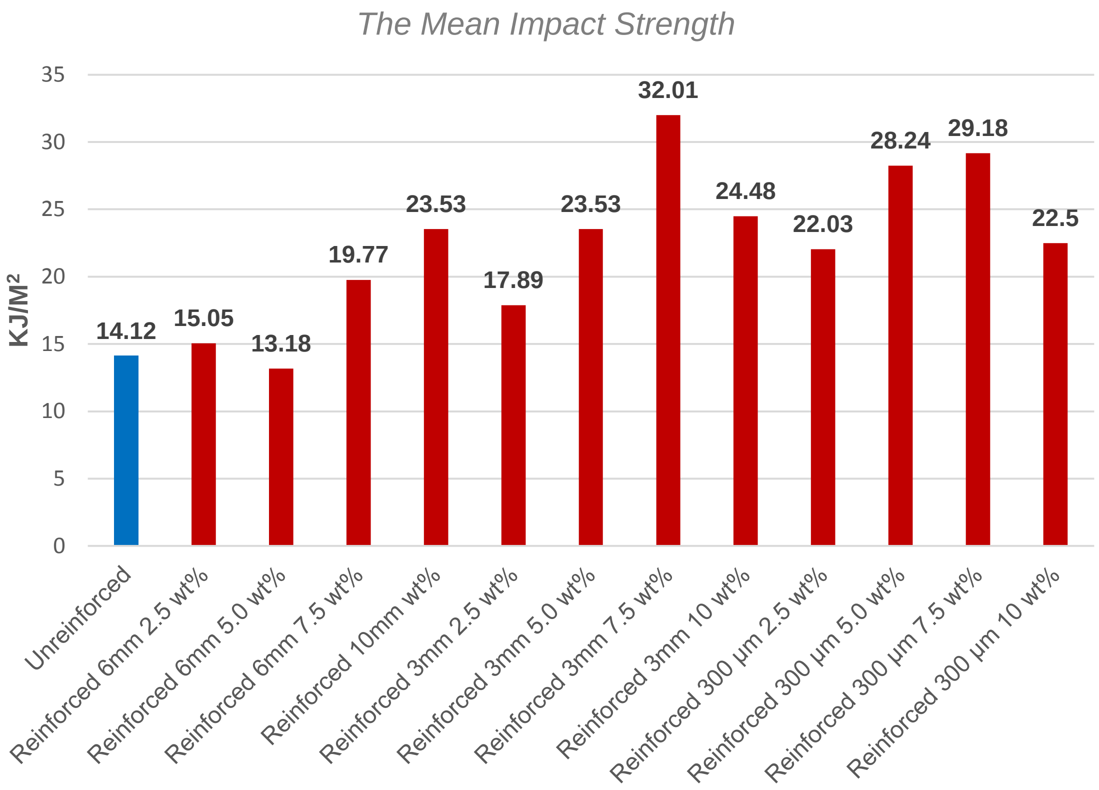
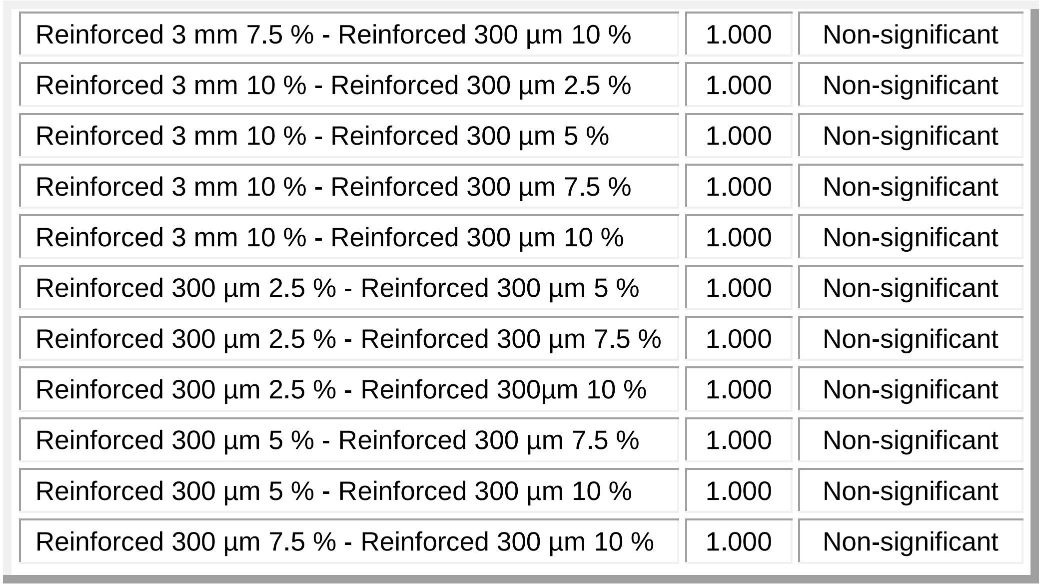


Figure 2: Mean impact strength (KJ/M^2) of the sample groups

Table 4: Bonferroni test for impact properties of unreinforced and *H. sabdariffa* fibre-reinforced denture base acrylic resins

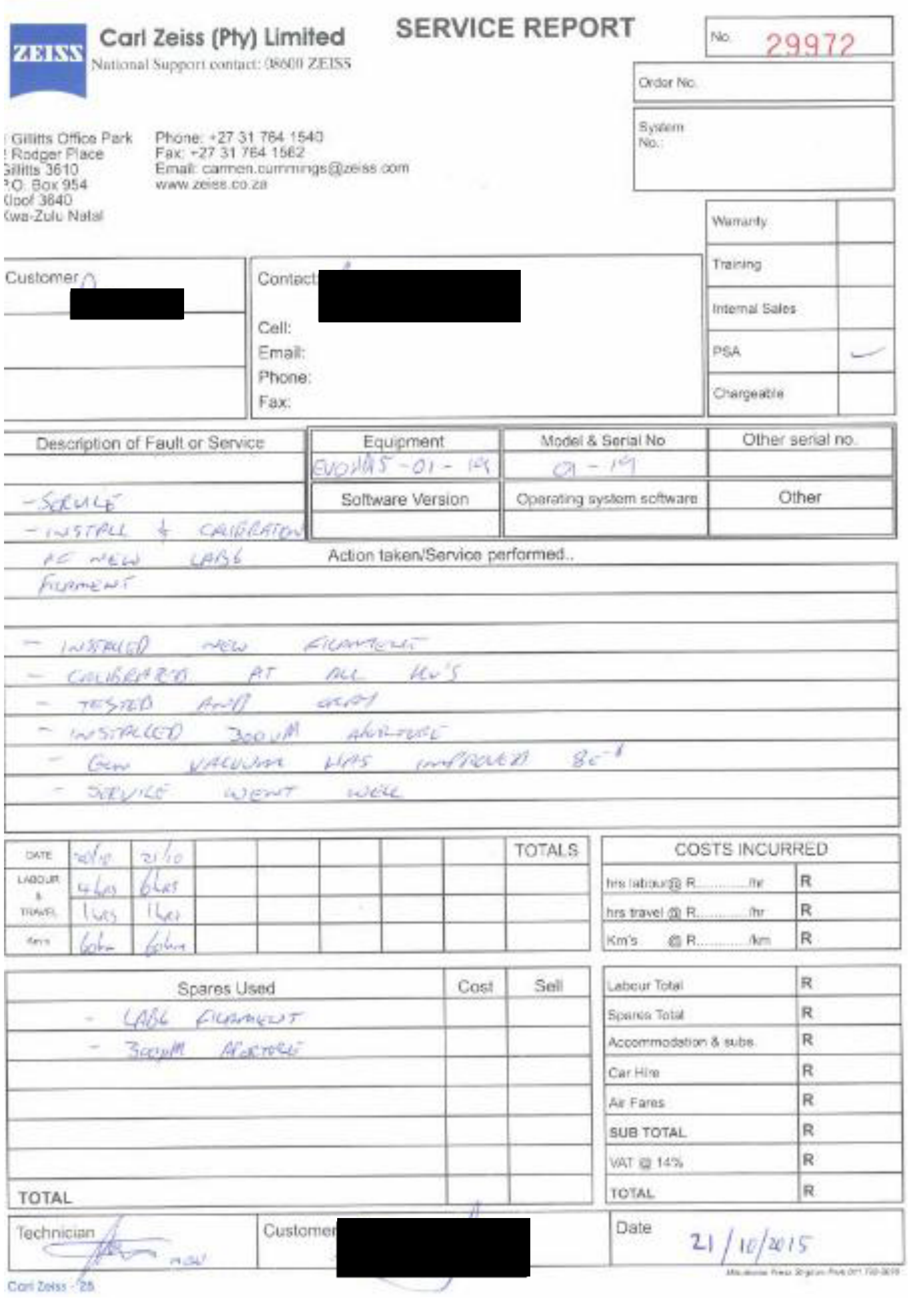
Groups comparison	P-value	Significance
Unreinforced - Reinforced 6 mm 2.5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 7.5 %	1.000	Non-significant
Unreinforced - Reinforced 6 mm 10 %	1.000	Non-significant
Unreinforced - Reinforced 3 mm 2.5 %	1.000	Non-significant
Unreinforced - Reinforced 3 mm 5 %	1.000	Non-significant
Unreinforced - Reinforced 3 mm 7.5 %	0.038	Significant
Unreinforced - Reinforced 3 mm 10 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 2.5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 7.5 %	1.000	Non-significant
Unreinforced - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 6 mm 5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 6 mm 7.5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 6 mm 10 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 3 mm 2.5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 3 mm 7.5 %	0.058	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6 mm 2.5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 6 mm 2.5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 6 mm 7.5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 6 mm 10 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 3 mm 2.5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 3 mm 7.5 %	0.025	Significant
Reinforced 6 mm 5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 300 µm 5 %	1.000	Non-significant

Reinforced 6 mm 5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6 mm 5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 6 mm 10 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 3 mm 2.5 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 3 mm 7.5 %	0.414	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6 mm 7.5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 3 mm 2.5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 3 mm 7.5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 6 mm 10 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 3 mm 5 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 3 mm 7.5 %	0.193	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 3 mm 2.5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 3 mm 7.5 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 3 mm 5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3 mm 7.5 % - Reinforced 3 mm 10 %	1.000	Non-significant
Reinforced 3 mm 7.5 % - Reinforced 300 µm 2.5 %	0.978	Non-significant
Reinforced 3 mm 7.5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 3 mm 7.5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant



Reinforced 3 mm 7.5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 3 mm 10 % - Reinforced 300 µm 2.5 %	1.000	Non-significant
Reinforced 3 mm 10 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 3 mm 10 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 3 mm 10 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 300 µm 2.5 % - Reinforced 300 µm 5 %	1.000	Non-significant
Reinforced 300 µm 2.5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 300 µm 2.5 % - Reinforced 300µm 10 %	1.000	Non-significant
Reinforced 300 µm 5 % - Reinforced 300 µm 7.5 %	1.000	Non-significant
Reinforced 300 µm 5 % - Reinforced 300 µm 10 %	1.000	Non-significant
Reinforced 300 µm 7.5 % - Reinforced 300 µm 10 %	1.000	Non-significant

Appendix 2: SEM Calibration Certificate



Carl Zeiss (Pty) Limited
National Support contact: 08600 ZEISS

SERVICE REPORT

No. 29972

Order No.

System No.:

Gillitts Office Park
Rodger Place
illitts 3610
O. Box 954
loof 3840
wa-Zulu Natal

Phone: +27 31 764 1540
Fax: +27 31 764 1562
Email: carmen.cummings@zeiss.com
www.zeiss.co.za

Warranty	
Training	
Internal Sales	
PSA	✓
Chargeable	

Customer [redacted]

Contact [redacted]
Cell:
Email:
Phone:
Fax:

Description of Fault or Service
- SERVICE
- INSTALL & CALIBRATION OF NEW LAB6 FILAMENT

Equipment	Model & Serial No	Other serial no.
EVO MA15 - 01 - 19	01 - 19	
Software Version	**Operating system software**	**Other**

Action taken/Service performed..
- INSTALLED NEW FILAMENT
- CALIBRATED AT ALL KV'S
- TESTED AND OKAY
- INSTALLED 300uM APERTURE
- GUN VACUUM HAS IMPROVED $8E^{-8}$
- SERVICE WENT WELL

								TOTALS
DATE	20/10	21/10						
LABOUR & TRAVEL	4hrs	6hrs						
	1hrs	1hrs						
Km's	60km	60km						

COSTS INCURRED	
hrs labour @ R............/hr	R
hrs travel @ R............/hr	R
Km's @ R............/km	R

Spares Used	Cost	Sell
- LAB6 FILAMENT		
- 300uM APERTURE		
TOTAL		

Labour Total	R
Spares Total	R
Accommodation & subs.	R
Car Hire	R
Air Fares	R
SUB TOTAL	R
VAT @ 14%	R
TOTAL	R

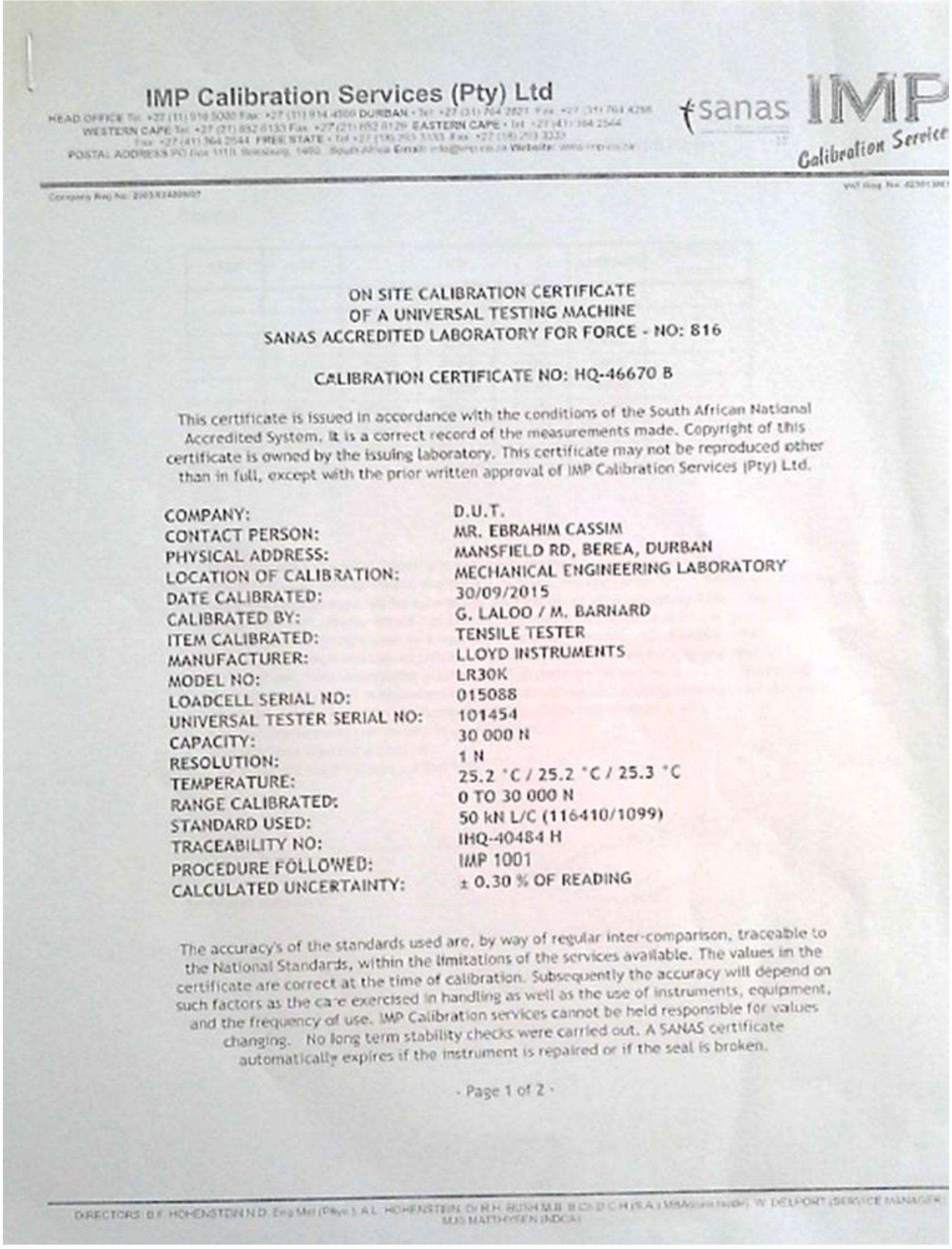
Technician

Customer [redacted]

Date 21/10/2015

Carl Zeiss - 25

Appendix 3: Calibration Certificate- LLOYD LR 30K



IMP Calibration Services (Pty) Ltd

ON SITE CALIBRATION CERTIFICATE
OF A UNIVERSAL TESTING MACHINE
SANAS ACCREDITED LABORATORY FOR FORCE - NO: 816

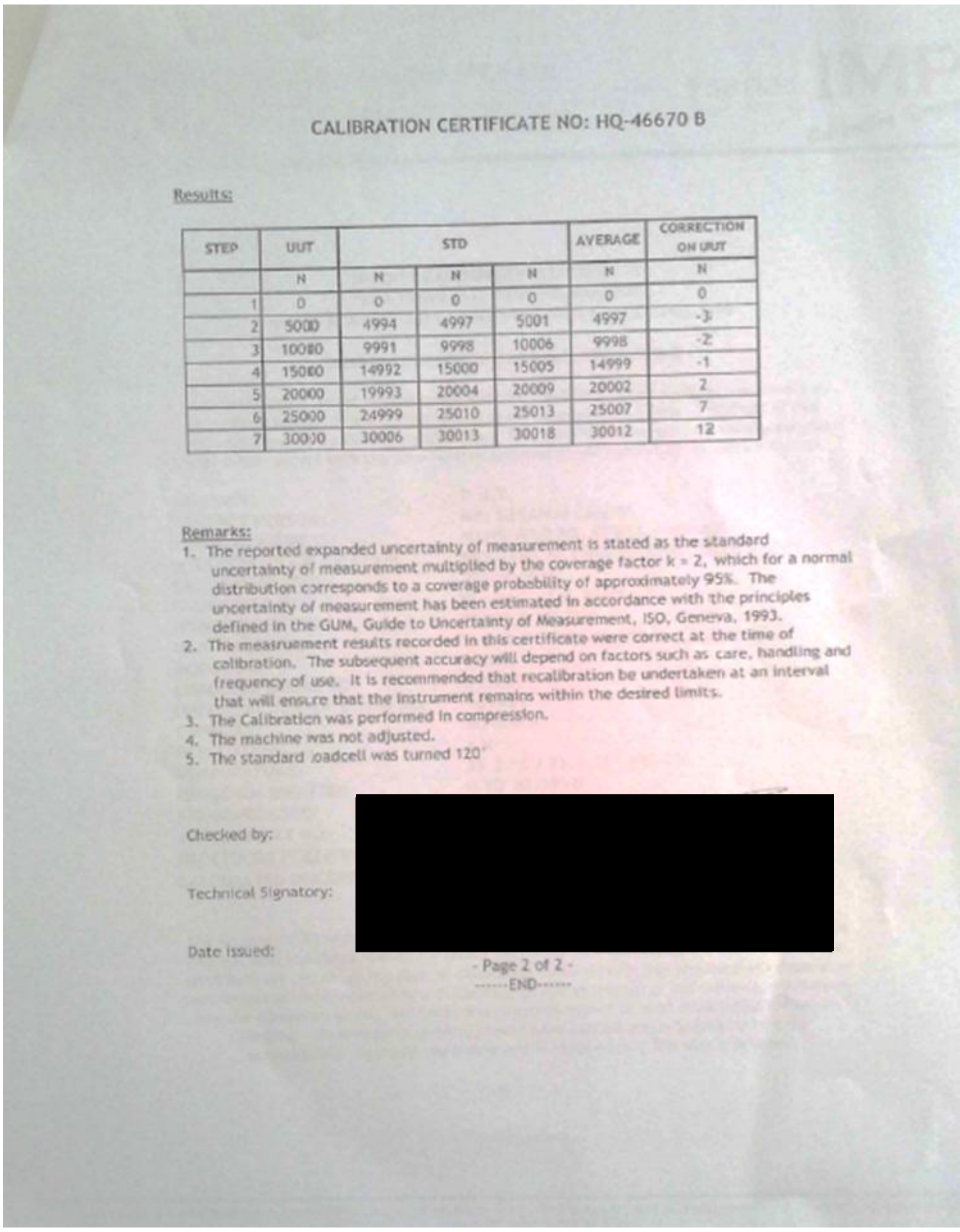
CALIBRATION CERTIFICATE NO: HQ-46670 B

This certificate is issued in accordance with the conditions of the South African National Accredited System. It is a correct record of the measurements made. Copyright of this certificate is owned by the issuing laboratory. This certificate may not be reproduced other than in full, except with the prior written approval of IMP Calibration Services (Pty) Ltd.

COMPANY:	D.U.T.
CONTACT PERSON:	MR. EBRAHIM CASSIM
PHYSICAL ADDRESS:	MANSFIELD RD, BEREA, DURBAN
LOCATION OF CALIBRATION:	MECHANICAL ENGINEERING LABORATORY
DATE CALIBRATED:	30/09/2015
CALIBRATED BY:	G. LALOO / M. BARNARD
ITEM CALIBRATED:	TENSILE TESTER
MANUFACTURER:	LLOYD INSTRUMENTS
MODEL NO:	LR30K
LOADCELL SERIAL NO:	015088
UNIVERSAL TESTER SERIAL NO:	101454
CAPACITY:	30 000 N
RESOLUTION:	1 N
TEMPERATURE:	25.2 °C / 25.2 °C / 25.3 °C
RANGE CALIBRATED:	0 TO 30 000 N
STANDARD USED:	50 kN L/C (116410/1099)
TRACEABILITY NO:	IHQ-40484 H
PROCEDURE FOLLOWED:	IMP 1001
CALCULATED UNCERTAINTY:	± 0.30 % OF READING

The accuracy's of the standards used are, by way of regular inter-comparison, traceable to the National Standards, within the limitations of the services available. The values in the certificate are correct at the time of calibration. Subsequently the accuracy will depend on such factors as the care exercised in handling as well as the use of instruments, equipment, and the frequency of use. IMP Calibration services cannot be held responsible for values changing. No long term stability checks were carried out. A SANAS certificate automatically expires if the instrument is repaired or if the seal is broken.

- Page 1 of 2 -



CALIBRATION CERTIFICATE NO: HQ-46670 B

Results:

STEP	UUT	STD			AVERAGE	CORRECTION ON UUT
	N	N	N	N	N	N
1	0	0	0	0	0	0
2	5000	4994	4997	5001	4997	-3
3	10000	9991	9998	10006	9998	-2
4	15000	14992	15000	15005	14999	-1
5	20000	19993	20004	20009	20002	2
6	25000	24999	25010	25013	25007	7
7	30000	30006	30013	30018	30012	12

Remarks:

1. The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95%. The uncertainty of measurement has been estimated in accordance with the principles defined in the GUM, Guide to Uncertainty of Measurement, ISO, Geneva, 1993.
2. The measruement results recorded in this certificate were correct at the time of calibration. The subsequent accuracy will depend on factors such as care, handling and frequency of use. It is recommended that recalibration be undertaken at an interval that will ensure that the instrument remains within the desired limits.
3. The Calibration was performed in compression.
4. The machine was not adjusted.
5. The standard loadcell was turned 120°

Checked by:

Technical Signatory:

Date issued:

[redacted]

- Page 2 of 2 -

------END------