Using eggshell for the development of a quality alternative material to pumice in reducing the surface roughness of heat-cured acrylic resins.

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Abstract

Pumice is used in the polishing of dental appliances to remove surface irregularities. It is usually used in a slurry form that is pumice powder mixed with water. In Nigeria, the increased cost of pumice as a result of its limited supply into the country has encouraged dental technicians to re-use pumice slurry for longer periods than advocated when polishing acrylic dentures, whether new or old dentures which have been worn in the mouth. Consequently, this is likely to increase cross-infection of communicable diseases in the dental technology laboratory. Although materials such as white sand, black sand and porcelnite can be used, literature documents that these materials are less effective in the polishing of acrylic dentures (Areeg 2011). The focus of this study was to use eggshells, a natural waste product, to develop and test the quality of an alternative material to reduce the surface roughness of heat-cured acrylic resins.

A quantitative research paradigm and an experimental research strategy were adopted. The research design included two phases. In phase one of this study, different characterisation techniques such as Brunnae-Emmer Teller (BET); Fourier Transform Infrared Spectroscopy (FTIR); X-ray Diffraction (XRD); Energy Dispersive X-ray Spectroscopy (EDX) and Scanning Electron Microscope (SEM); Transmission Electron Microscopy (TEM); Laser Scattering Particle Size Distribution Analyser (PSA); Thermo-Gravimetric Analysis (TGA); and Induction-Coupling-Optical Emission Spectroscopy (ICP-OES) were used to assess the suitability of the new abrasive material (NAM). In addition, the level of microbial contamination of the NAM was assessed in line with the specified microbial limits for cosmetic products. In contrast, phase two investigated the product-based quality of the NAM as an abrasive material for removable dental appliances. There were two sample groups, that is, the NAM (test group) and Pumice (control), and each sample group had 50 PMMA acrylic specimens. The surface roughness (R_a) was measured using a Talysurf profilometer. An Independent Tukey test was used to analyse the R_a values (p=0.05). A Scanning Electron Microscope (SEM) and Optical Microscope (OEM) were further used to support the results of the profilometer in terms of the quality of surface finish and polish. Validity of the study was achieved following the ISO 20795-1 (2013) methods

of preparation and fabrication of the acrylic specimens. The reliability was determined via reproducibility and repeatability of tests.

The BET analysis showed that the NAM is predominantly a mesoporous powder. The FTIR and XRD analyses confirmed that the NAM is pure calcite with unique water absorbing characteristics, and is free of bacteria. The EDX and ICP-OES analyses revealed calcium, oxygen and carbon as the major elemental composition of the NAM. The SEM and TEM images revealed irregular shaped particles in the NAM. The PSA analysis of the particle distribution showed the NAM to be superfine (50nm to 0.3µm) and medium (44µm powder), respectively. The TGA analysis revealed a high-grade carbonate product in the NAM (>66.0 mass% of calcium carbonates). In addition, and in terms of in the qualities of the NAM in reducing the surface roughness of PMMA resins, the test group and the control group produced R_a values that were significant different ($p<0.0001$). The SEM and OEM analyses further confirmed the differences in the surfaces between the polished sample groups at different magnifications. Overall, the control showed the highest mean average (0.1056±0.03688µm), whereas the test group had the lowest R_a values (0.0476±0.01379).

The lowest R_a values measured with the test group indicated that the NAM improves the surface smoothness of PMMA acrylic specimens. Notably, this study conclusively showed that the NAM effectively reduces the surface roughness to below the threshold limit value of 0.2µm. Significantly, and in associating the R_a values to the threshold limit value of 0.2µm, the NAM produced better results than pumice. Hence the use of the NAM as a polishing material for acrylic dentures is highly recommended. Finally and in line the NAM being a suitable alternative to pumice as it effectively reduces the surface roughness of PMMA specimens, future investigation into the use of eggshell nanoparticles to develop dental prophylaxes will be encouraged.

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Declaration

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CONFERENCE PAPER PRESENTED ARISING FROM THIS STUDY

Onwubu, S.[1], Vahed, A.[2], Singh, S.[2] and Kanny, K[3]. **2015**. Title: Characterisation of eggshells as a dental abrasive material. In: proceedings of *2nd International Conference on Composites, Biocomposites and Nanocomposites conference proceedings.* Durban, 203-220.

JOURNAL PAPERS SUBMITTED ARISING FROM THIS STUDY

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_________________ _________________

Signature Date

Dedication

Dedicated to my loving parents, Mr and Mrs Sylvester Onwubu. Your love and support inspired in me the pursuit of excellence and the desire to learn more.

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Acronyms

ADTN	Association of Dental Technologists of Nigeria
ANSI/ADA	American National Standards/American Dental Association
ASTM	American Society for Testing and Materials
BET	Brunnae-Emmer Teller
CFU	Colony Forming Units
CSIR	The Council for Scientific and Industrial Research
DEPA	Danish Environmental Protection Agency
DUT	Durban University of Technology
EDX	Energy Dispersive X-ray Spectroscopy
FEPA	Federation of European Abrasive Producers
FDA	Food and Drug Administration
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Performance Liquid Chromatography
ICP-OES	Inducting Coupling Plasma – Optical Emission Spectroscopy
IEC	International Electrotechnical Commission
IREC	Institutional Research Ethics Committee
IUPAC	International Union of Pure and applied Chemistry
ISO	International Standard Organisation
LAS	Linear Alkyl Benzene Sulfonate
NA	Nutrient Agar
NAM	New Abrasive Material
PDA	Potato Dextrose Agar
PMMA	Poly Methyl Methacrylate Acrylic
PSA	Particle Size Distribution Analyser
OEM	Optical Electron Microscope
RPM	Revolution per Minute

SEM	Scanning Electron Microscopy
SPSS	Statistical Package for Social Science
TEM	Transmission Electron Microscope
TGA	Thermo-Gravimetric Analysis
UKZN	University of KwaZulu-Natal
XRD	X-ray Diffraction

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Chapter One - Introduction

1.1 Background and context of the Study

In Nigeria there is a limited supply of pumice, which is an abrasive material commonly used to polish heat-cured poly methyl methacrylate acrylic (PMMA) dentures. Consequently, the cost of purchasing pumice in Nigeria has increased considerably to such an extent that in a personal communication on the 5 March 2014 the President of the Association of Dental Technologists of Nigeria (ADTN), Okeke, indicated that in an attempt to save costs Dental Technicians in Nigeria are re-using pumice slurry (pumice powder mixed with water) for longer periods to polish new and old repaired PMMA dentures. This adversely contributes to cross-infection in the dental technology laboratory, as pumice is likely to be contaminated from the various polishing processes. Hence, the limited supply of pumice and the associated factor of increased cross-contamination in the dental laboratory prompts this study to develop an alternative material to pumice by using eggshells.

Several authors (Tombak 2006; Henuset 2011; King'Ori 2011; Bee 2012) maintain that the calcium of eggshells is similar to bone and teeth, hence it is used in certain toothpastes as an abrasive cleaner for dental plaque. Similarly, and as Henuset (2011) explained, the calcium of eggshells supports its use in the manufacture of abrasive paper, abrading wheels, bands, and disks. This suggests that eggshells could potentially be used in the development of a dental abrasive and polishing material to help in reducing the surface roughness of dental prostheses. There appears to be very little research, however, on using eggshells as an alternative abrasive material to pumice in the polishing and finishing of PMMA dentures. This study will endeavour to develop an alternative material where eggshells are the main constituent of the new abrasive material (NAM). The acronym 'NAM' will therefore be consigned to the new abrasive material for the rest of this dissertation.

1.2 Problem Statement

The re-use of pumice slurry to polish new and old repaired PMMA dentures has promoted high levels of cross-contamination in the dental technology laboratory, as reported by several researchers (Kugel *et al*. 2000; Agostinho *et al*. 2004; Jafari *et al*. 2006; Vojdani and Zibaei 2006; Amaal 2011; Firoozeh *et al.* 2013).

In attempting to address the re-use of pumice slurry as a potential source of contamination in dental laboratories in Nigeria, this study will use eggshells to develop an alternative abrasive material to pumice. Equally important and from an environmental sustainability and management perspective, using the NAM to polish dental appliances strengthens the economic benefits associated with using natural waste material, which is high on the global agenda for a greener environment. Part of this enquiry is to further ensure that the new developed material complies with the international standards for quality management and quality assurance (ISO 9001 or equivalent). Ultimately, and in line with criteria recommended by Foster (2012), this will ensure that the new dental abrasive material is safe to use, affordable, reliable, and of good quality to meet its intended purpose.

1.3 Aim of the Study and Research Objectives

The aim of this study is to develop and test the quality of an alternative material (eggshells) to pumice, for reducing the surface roughness of heat-cured acrylic resins.

Research Objectives: The objectives of this study are in two phases, namely:

1.3.1 Phase One: The development of the New Abrasive Material (NAM).

1.3.1.1 To determine the physical characteristics of the NAM in terms of crystallisation; hardness; pore volume; particle size and surface area; to establish the abrasive and strength qualities of the material.

1.3.1.2 To determine the levels of degradability and stability of the material by conducting thermal analyses of the NAM.

1.3.1.3 To establish the level of bacterial contamination in order to ascertain the microbial contents of the NAM.

1.3.1.4 To determine the chemical constituents of the NAM in order to identify the different metal ions.

1.3.1.5 To determine the production costs of developing the NAM in comparison with pumice.

1.3.1.6 To compare and evaluate the hardness, particle size, and shape of the NAM and pumice by using the American National

Standards/American Dental Association (ANSI/ADA) and the American Society for Testing and Materials (ASTM).

1.3.2 Phase Two: To establish the product-based quality of the NAM in terms of 'fitness for purpose'.

1.3.2.1 To measure the surface roughness of heat-cured acrylic resin specimens by using a profilometer in order to determine the effectiveness of the NAM as an abrasive material in comparison with pumice.

1.3.2.2 To examine the surface characteristics of heat-cured acrylic resin specimens polished with the NAM by using a scanning electron microscope (SEM) in order to ascertain its quality as an alternative abrasive material in comparison with pumice.

1.4 Research Hypothesis

H_0: The new abrasive material is not a suitable alternative pumice as it does not reduce the surface roughness of PMMA specimens.

H_1: The new abrasive material is a suitable alternative to pumice as it effectively reduces the surface roughness of PMMA specimens.

1.5 Rationale/Significance of the Study

The pursuit of alternative abrasive materials to pumice has generated some research (Maalhagh-Fard *et al.* 2003; Alaa-ezit 2006; Bassam, Alaa and Wael 2008; Srividya, Chandrasekharan and Jayakar 2011). Areeg (2011) recently reported that the mechanical and physical properties of common alternative abrasive materials such as white sand, black sand, and porcelnite were less effective than pumice in smoothing the surface roughness of PMMA resins. Studies have indicated that the calcite form of calcium carbonate ($CaCO_3$) is the main abrasive constituent in dental dentifrice (toothpaste) as it is effective in keeping teeth clean and healthy (Craig, Powers and Wataha 2000; Manappallil 2003; Collins *et al.* 2005; Lynch, Bebington and ten Cate 2005; Joiner 2006; Schemehorn, Moore and Putt 2011; Anusavice and Antonson 2013; Waterfield 2013). This mineral, which is generally mined from rocks (Boron 2004; Oliveira, Benelli and Amante 2013), is naturally present in eggshells (95% by weight). In light of $CaCO_3$ being recognised for its abrasive properties in dentifrices, this study aims to develop an alternative abrasive material to pumice using eggshells.

1.6 Assumptions

The following assumptions are made in relation to this study:

- The researcher has a B Tech: Dental Technology qualification, hence he has sound laboratory knowledge and experience to polish heat-cured acrylic resins.
- All data collection instruments are valid and reliable based upon their frequent use and calibration period at various universities.
- The new abrasive material is cheaper than pumice, hence it will be a more viable option for dental technicians.

1.7 Delimitation

Regardless of the many brands of heat-cure acrylic resins available in South Africa, this study will only use Vertex™ (Netherlands) heat-cure acrylic resin material. Vertex™ was selected as a heat cured acrylic for this study because it is the product used in the Dental Laboratory at Durban University of Technology Laboratory. It must be noted that irrespective of the brand name, this acrylic conforms to the ISO 1567 (1999), which is the equivalent of ANSI/ADA specification 12 of denture base resins, which are the recommended standards for dentures. Hence, Vertex™ heat-cured acrylic resin is deemed appropriate for the study.

1.8 Structure of the Thesis

The thesis will be divided into five chapters. Chapter one foregrounded the context of the study by detailing the reasons for developing an alternative material to pumice. This steered the chapter towards the aim and objectives, hypothesis, assumptions, delimitations and scope of the study.

Chapter 2 presents an overview of the literature on abrasive materials used for polishing. This will include a discussion on the abrasive characteristics of pumice and its application as a polishing material in dental laboratories. Subsequently, the introduction and review of eggshell and its use as an abrasive material follows.

Chapter 3 describes the research design and methodology by detailing the quantitative research paradigm and experimental research design that is to be adopted in this study. This will include an explanation of the pilot study and main study.

Chapter 4 presents the results on the abrasive characteristics of the NAM and pumice. Tables, graphs and images will support the analytical results. Overall, this chapter will provide a rigorous discussion on the NAM and pumice by comparing the surface roughness value measured on the polished PMMA specimens.

Chapter 5 forms the final chapter and will provide the conclusions drawn from the study. It will also identify any limitations and consider future directions for this research.

Chapter Two - Literature Review

This chapter reviews literature related to abrasive materials used for polishing poly methyl methacrylate (PMMA) dentures. The review introduces pumice as an abrasive material and explains its abrasive characteristics in terms of particle size, hardness and shape. Subsequently, eggshell and its use as an abrasive material will be discussed. Overall this literature review is structured into five sections. Section one discusses the physical characteristics of pumice and its application as an abrasive material for polishing and finishing of dental prostheses. Section two describes the physicochemical characteristics of eggshells. It is anticipated that this will help to support the development of the NAM as an alternative material to pumice. A discussion follows on the different quality standards (International Standard Organisation ISO 9001: 2008; American National Standards/American Dental Association ANSI/ADA standards 1986, and American Society for Testing and Materials ASTM standards C136 2006), which is the underpinning theory in the development of the NAM. It is envisaged that understanding the physiochemical characteristics of eggshells, particularly as they relate to its particle size distribution, will help in characterising eggshell powder as a potential dental abrasive material. The chapter concludes with an evaluation of the overall cost to develop the NAM, particularly as it is a critical factor in introducing and promoting the abrasive material to the Dental Technology industry.

2.1 The Abrasive Characteristics of Pumice

Several studies (Uğur 2003; Alaa-ezit 2006; Bassam, Alaa and Wael 2008; Areeg 2011; Srividya, Chandrasekharan and Jayakar 2011; Hess 2014) have reported on pumice in terms of its chemical constituents, physical (hardness and particle size) and mechanical characteristics (porosity; crushability; and light weight). According to Turhan and Gunduz (2008: 332) the powdered form of volcanic rock is called pumice and comprises of 60-67% Silica (SiO_2), 13-17% Alumina (Al_2O_3), 7-8% Sodium oxide-Potassium oxide (Na_2O-K_2O), with minimal amounts of Iron oxide (Fe_2O_3), Calcium oxide (CaO), and Titanium Dioxide (TiO_2). As reported by Li, Yang and Zuo (2010) and Orense and Power (2013), the physical characteristics of pumice enables it to be crushed and compressed into powder. Consequently this has promoted its use as an abrasive polisher, particularly in reducing the surface roughness of PMMA dentures and orthodontic base plates.

Significantly, Quirynen and Bollen (1995) and Al-Kheraif (2014) reported that using pumice (coarse CL-60) to mechanically smooth PMMA dentures produces a surface roughness less than the threshold value of 0.2µm, thereby reducing the retention of food debris and bacteria on PMMA dentures. In turn, and as indicated by other authors (Kuhar and Funduk 2005; Moura *et al.* 2006; Satpalty, Dhakshaini and Gujjari 2013), plaque formation together with its negative effects on both the teeth and periodontal tissues is further minimised. This aligns with Anusavice and Antonson (2003; 2013), Morgan (2004) and Rahal *et al.* (2004), where the 0.2µm threshold value was shown to be an important indicator for patient comfort and denture longevity. The work by the aforementioned authors therefore suggests that developing an alternative abrasive material using eggshell is important to smoothen dentures processed with PMMA.

According to Areeg (2011: 51) and Bassam, Alaa and Wael (2008: 283) the physical properties of an abrasive material, such as particle size and hardness, are directly proportional to the quality of the surface roughness. Similarly, and as explained by Anusavice and Antonson (2013), the strength of an abrasive material relates to the hardness of the material. They defined hardness as the resistance of a material before it is plastically deformed by being indented or scratched by another material. Hence, if an abrasive material is too hard, or if the particle size is very coarse, the quality of the surface roughness will be affected as deep scratches result. This study will take cognisance of the particle size when developing the NAM.

Additionally, Anusavice and Antonson (2013) argued that if an abrasive material does not have the correct particle shape, or does not break down into newly sharp-edged particles, the quality of the polishing materials will be compromised. This is consistent with Bassam, Alaa and Wael (2008), who demonstrated that smaller particle sized abrasive materials facilitates the polishing mechanisms by rapidly wearing away surfaces to expose newly-formed sharp materials needed to decrease surface roughness.

O'Brien (1997; 2002) and Manappallil (2003) also maintained that irregular sharp particles abrade surfaces more rapidly than more rounded particles, which leave duller cutting angles. The advice of the aforementioned authors will be considered when developing the NAM. It is noted that particle shape is dependent upon the ball milling process and cognisance is taken of the abrasion of these particles will cause on the surfaces.

Although pumice effectively smoothens denture surfaces, Bassam, Alaa and Wael (2008) contend that the amount of surface smoothness depends on the variation in the mineral composition of pumice. They elaborated that different companies produce pumice of different surface roughness values. This suggests that the characteristics of pumice such as particle size are an important factor in terms of producing a PMMA denture with a high polish. This resonates with the work conducted by Rizzatti-Barbosa *et al.* (2006: 979). They explained that finer particle sized pumice improves surface smoothness, and promotes a higher shine, of PMMA dentures. The next section will therefore review the characteristics of eggshell, particularly its particle size.

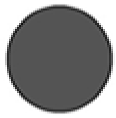
2.3 Physicochemical Characteristics of Eggshell

Generally, and as posited by Giron (1998;2002), Daengprok, Garnjanagoochorn and Mine (2000), Jay (2000), Campos *et al.* (2004), and Cardosa *et al.* (2005), eggshells are texturally hard and porous as they protect the chicken embryo from microorganisms. According to Freire and Holanda (2006: 244) the porousness of eggshells makes it possible to crush them to various particle sizes ranging from 2 to 900 microns (µm). Consequently, the eggshell powder that is produced can be widely used as an abrasive material. Furthermore, and as explained by Henuset (2011), the temperature and time taken to process eggshells into powder changes its chemical and physical properties. He asserted that the chemical composition of eggshells, particularly the calcite of the calcium carbonate, contributes to the abrasive properties. Importantly, and as Siriprom *et al.* (2014) demonstrated, the properties of eggshell changes when heated at 900°C. Oxides are released, thereby changing the structure of calcium carbonate. Their work corroborates with Murakami *et al.* (2007), who asserted that calcium carbonate maintains stability up to 600°C, however between 601°C and 770°C carbon dioxide, and subsequently calcium oxide, is released. The aforementioned heating temperatures will be considered when developing the NAM.

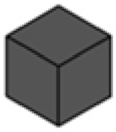
In addition, and resonating with Mitchell (2005) who found that the high calcium content make eggshells insoluble in water. Brand-Garnys (2014) recently demonstrated that calcium carbonate does not dissolve easily in water. Oliveira, Benelli and Amante (2013) and Rahman *et al.* (2014) have therefore advised adding sodium lauryl sulfate to eggshell powder to improve its solubility in water. Their advice supports the argument of several studies (He and Yalkowsky 2006; Remenar *et al.* 2007; Aburub, Risley and Mishra 2008; Seedher and Kanojia 2008; Li, Qiao and Wang 2013), which indicated that sodium lauryl sulfate helps to increase solubility and dissolution rates of pharmaceutical products. The advice given by the aforementioned authors is pertinent to this study, particularly in terms of ensuring that the NAM is 'fit for purpose'. In terms of particle size, Chen (2008) showed that eggshells crushed to particle sizes between 0.1µm to 10nm produced an ultra-fine powder that was used in toothpastes and cosmetics. Tsai *et al.* (2008) also reported that eggshells crushed into finer powder promotes its use in biomaterial fields. Recently, Brand-Garnys (2014) revealed that eggshell particles between 74µm and 595µm are abrasive agents in skin-care products. This study therefore intends to use different particle sizes when developing the NAM, in accordance with the various quality standards such as ANSI/ADA specification No. 37 (1986) and ASTM C13 (1996; 2006).

Apart from the particle size, and as asserted by Lowell *et al.* (2004), the physical properties of powder materials are influenced by its shape and degree of porousness. Stachowiak *et al.* (2005) elaborated that the shape of the abrasive powder (Figure 1) is directly proportional to the abrasive wear rate, which is an important factor when describing particle angularity or sharpness. Their report corroborates with the earlier work of Mikli *et al.* (2001), who confirmed that an increase in particle angularity simultaneously increases the abrasive wear rates. This study will be characterising the particle shape of the NAM, as it directly influences the rate of abrasion.

Angular: Shape edged or having roughly polyhedral shape.



Spherical: globe shaped



Cubic

Rounded (or Modular): Having rounded, irregular shape

Spongy/Irregular: Lacking any symmetry

Flakey: Plate-like

Cylindrical/Crystalline: Freely developed in a fluid medium of geometric shape

Acicular: Needle-shaped

Other Shapes:

Flakey: Regularly or irregularly thread-like.
Granular: Having approximately an equidimensional irregular shape.

Figure 2-1: Characterisation on the shape of abrasive powders (adapted from Groover (2002)).

2.4 Microbial Content of Eggshell

Shawkey, Pillai and Hill (2003) and Sweeney, Lovette and Harvey (2004) emphasised that incubating eggshells potentially reduces the build-up of harmful microorganisms. Consistent with them, Cook *et al.* (2005) maintained that incubation reduces humidity and precipitation, thereby minimising the survival of most pathogenic micro-organisms. Hence, eggshells to be used in this study will be thermally treated.

According to Suzuki *et al.* (2006: 1) thermal treatment of eggshells at temperatures around 350°C prevents the growth of bacteria such as *Pseudomonas*, *Listeria*, *Monocytogenes*, *E-coli* yeast, and Lactic acid. They further reported that eggshells heated around 350°C converts zinc carbonates to zinc oxides. This effectively acts as an antibacterial agent. Suzuki *et al.* (2006) further showed that heating eggshells at 600°C converts magnesium carbonate to magnesium oxide, which functions as a bacteriostatic agent. Equally important, and as reported by several authors (Radkowski 2002; Hardy 2004; Botey-Salo *et al.* 2012; Gole *et al.* 2014), the growth of *salmonella* on eggshells, which is the main cause of food poisoning, increases at lower temperatures. Contaminated environments exacerbate the transmission of *salmonella* through the pores of eggshells, as posited by Fajardo *et al.* (1995), Miyamoto *et al.* (1998), and Aygun, Sert and Copur (2012). Hutchison *et al.* (2004) and Messens *et al.* (2011) believed that washing eggshell reduces salmonella contamination, however Gole *et al.* (2014) showed that the survival rate of *salmonella* on washed and unwashed eggshell surfaces was more or less the same. This is consistent with the earlier work by Kim and Slavik (1996) and Wang and Slavik (1998), where using inappropriate chemicals to wash eggshells promoted pathogenic bacteria to penetrate the surfaces of eggshells. Significantly, and in line with other studies (Zeidler 2001; Hutchison *et al.* 2003; Hutchison *et al.* 2004), eggshells should therefore be washed with clean water containing detergents and a commercial chlorine compound to reduce microbial growth.

The methods of washing and thermal heating of eggshells is imperative to the development of the NAM. Additionally, Musgrove *et al.* (2004; 2005), Harbrecht and Bergdoll (2006) and Chousalkar *et al.* (2010) reported that *E-coli*, a toxin-producing bacteria, is present in crushed unwashed eggshells. In order to evaluate the presence of *salmonella* and *E-coli*, and in line with the International Standard Organisation (ISO

21149 and 16212); the Danish Environmental Protection Agency (DEPA) (Detmer *et al.* 2010); the Chinese Medicine Board (2004) guidelines for product safety; and the Food and Drug Administration (FDA) (2001), microbial testing of the NAM will be conducted. The aforementioned quality standards will be used in the preparation of the NAM and will provide the point of departure for the next section.

2.5 Standards for Powdered Abrasive Materials

The ANSI/ADA (1986) standards manual provides a uniform means of categorising and labelling all powdered abrasive used for dental purposes. This is done according to the distribution of particle size. The manual also outlines the various types of pumice that are used intraorally as dental prophylaxes for polishing tooth enamel, as well as in the polishing and finishing of dental prostheses. Anusavice and Antonson (2013: 238) have broadly categorised four particle sizes of abrasive materials, namely: coarse; medium coarse; medium fine and superfine. In reviewing the literature on particle size, and as illustrated in Table 2, it is worth nothing that there are subtle differences in particle size between these categories. The ASTM E11-04 (2004) covers the requirement for design and construction of testing sieves using a medium wire cloth (Figure 2-2), mounted in a frame for use in classification of abrasives materials according to designated particle size. This will be considered when sieving the NAM.

Table 2-1: Particle size categories of abrasive materials.

Particle Size	ASTM C136 (1996; 2006)	Federation of European producers of Abrasives (FEPA 32 F: 1971)	ANSI/ADA and O'Brien's criteria (1997; 2002)
Very coarse		1.68-2.83mm	
Coarse	0.50-1.19mm	1.00-1.41mm	100-500 µm
Medium	0.15-0.40mm	0.30-0.40mm	10-100 µm
Fine	0.045-0.18mm	0.13-0.18mm	0-10 µm
Very fine	0.008-0.047mm	0.003-0.004mm	

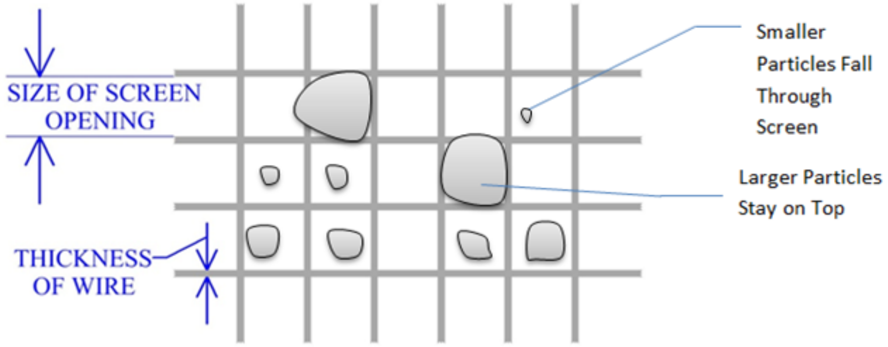


Figure 2-2: Screen mesh for characterising particle sizes (adapted from Groover (2002)).

With reference to hardness, Chandler (1999) and Marinescu *et al.* (2013) have reported that there are no known standards for hardness available for abrasive materials. Consequently, O'Brien (2002), Manappallil (2003) and Anusavice and Antonson (2013) therefore proposed that the abrasive material be harder than the substrate as a useful guideline to facilitate efficient polishing and finishing. Equally important, Anusavice and Antonson (2013: 238) recommended using a Mohs, Knoop's, or Vicker's hardness test, while O'Brien (1997; 2002) advised using a Brinell hardness test to determine the hardness value of dental abrasives. Furthermore, the seminal work of Friedrich Mohs (invented in 1820), a German mineralogist, ranked ten minerals from one to ten based on their scratch resistance in relation to one another (Table 2). Contrary to this, Anusavice and Antonson (2013) suggested using Knoop and Vicker tests to quantify the hardness of materials, which involves applying an indenter into the surface of a material under a known load (usually 100 Newtons). Subsequently, the depth of surface penetration determines the hardness value measured in units of force per unit area. The different hardness instruments will be considered when testing the hardness of eggshells.

Table 2-2: Comparison of hardness values of dental materials and abrasives.

Material	Hardness value			
	Mohs Hardness	*Knoop hardness (Kg/mm^2)*	*Vickers hardness (Kg/mm^2)*	*Brinell hardness (KgF)*
Talc	1	-	-	
Gypsum	2	-	12	-
Denture base resin	2-3	20	-	-
Calcite	3	135	-	
Dentine	3-4	70	57-60	48
Tripoli	6	-	-	-
Pumice	6-7	460-560	-	-
Porcelain	6-7	560	430	-
Tin oxide	6-7	-	-	-
Sand	7	-	-	-
Cuttle	7	800	-	-
Quartz	7	820	-	600
Zirconium silicate	7.5	-	-	-
Garnet	8-9	1,350	-	-
Corundum	9	2,000	-	-
Diamond	10	7,000--10,000	-	Above 5,000

2.6 NAM: Validating 'fitness for purpose'

Trullols (2006: 26) asserted that the process of assessing the performance criteria of any material relates closely to the concept of 'fitness of purpose'. The International Union of Pure and Applied Chemistry (1998) (in the orange book) defines this as the "….degree to which data produced by measurement process enables a user to make technically and administratively correct decisions for a stated purpose”. Similarly, and as van der Vleuten *et al.* (2012) moots, ‘fitness for purpose’ is a functional definition of quality as it refers to the concept of contributing to the achievement in assessment of quality of a product. In order to validate the product-based quality of the NAM in terms of ‘fitness for purpose’, analytical evidence by way of measuring the surface roughness of polished PMMA will provide … “confirmation that the product meets its intended use” (International Standard Organisation 2005).

Significantly, Anusavice and Antonson (2013) elaborated that the quality of the surface finish and polish can be characterised by the measuring the surface roughness of a PMMA using a profilometer, an optical microscope, or a SEM. In the last decade, literature has documented the wide use of the profilometer in measuring surface roughness (Bassam, Alaa and Wael 2008; Corsalini *et al.* 2009; Abuzar *et al.* 2010; Areeg 2011; Srividya, Chandrasekharan and Jayakar 2011; Dutta and Maria 2012) thereby supporting its use in this study. Field (2012: 25) described that profilometry can measure the surface roughness directly or indirectly using a contacting stylus and a laser profilometer, respectively. It is worth noting that the current ISO 5436-1 (2001) advised using the stylus profilometer. Stachowiak, Batchelor and Stachowiak (2004), Abuzar *et al.* (2010), and (Srividya, Chandrasekharan and Jayakar 2011) explained that stylus profilometry measurement involves traversing the surface with a diamond-tipped stylus, usually at a fixed radius 1.5-2.5µm. As highlighted by the ISO 3274 (1975) standard manual, the chisel-point tips (0.2µm x 2.5µm) are mainly used for detecting raised areas on a surface, whereas the conical tips are almost exclusively used for micro-roughness measurement. Stachowiak, Batchelor and Stachowiak (2004) also reported that the loading weight on the stylus ranges from 0.05-100mg. The surface roughness of the PMMA specimens in this study will be measured using a contact stylus profilometer. Essentially, this will validate one of criteria product quality of the NAM in terms of its ‘fitness for purpose’.

Furthermore, Abuzar *et al.* (2010) observed that the vertical displacement of the stylus is measured as the surface variation, usually measuring from 10nm to 1mm. Field (2012) showed that the vertical motion is dragged across the surface and is transformed into an analogue/digital signal. Consequently, the stylus is in perpetual contact with the surface that is being measured. Although this is often an advantage where a large vertical range is possible (typically 2µm to 250µm) there is a risk, however, of the diamond tip causing damage to the specimen. Silikas *et al.* (2005), Teixeira *et al.* (2005), Attin (2006), and Janus *et al.* (2010) advised that to maximise the way in which surface characteristics are reported a combination of more than one technique should be used. Consistent with them, Kuhar and Funduk (2005) and (Santos, Soo and Petridis 2013) also advocated using combined techniques. For example, this study will be using a profilometer and SEM to strengthen the assessment of the 'fitness for purpose' of the NAM.

According to Field (2012: 31) SEM involves the scattering of electrons at the specimen surface and the resulting signal received provides information about the surface topography and composition. He asserted that SEM images have a large depth of field (all parts of the image are in focus, despite their different depths) and can therefore yield high resolution 3-D images. For conventional SEM, and as propounded by Faria *et al.* (2008), the surface must be coated with a material that is electrically conductive to prevent the accumulation of electrostatic charge. This material is usually gold, and the specimens will undoubtedly be irreversibly altered during the desiccation and sputtering process. Gold–sputtering the specimen is pertinent to this study, particularly when microscopically characterising the PMMA specimens.

2.7 Quality Management and Assurance of NAM

Quality assurance is a way of preventing defects in a product, while simultaneously avoiding problems when the product is used for its intended purpose. The ISO 9000 (2005) pointed out that quality assurance is part of quality management focused on providing confidence of the of product quality. Quality management therefore subsumes 'fitness for purpose' as it ensures superior quality products and service delivery. There are quality parameters that therefore need to be considered when developing the NAM.

Garvin (1984 cited in Foster 2012) found that most definitions of quality were either transcendent, product-based, user-based, manufacturing-based, or valued-based. Transcendent quality, by contrast, is something that is intuitively understood but nearly impossible to communicate, such as beauty or love. He further described that product-based quality is found within the components and attributes of a product, whereas user-based quality depends on the customer's satisfaction. If the customer is satisfied, then the product is of a good quality. From a manufacturing perspective, Garvin (1984 cited in Foster 2012: 5) defined quality of a product as conforming to the design specifications thereby making it a product of good quality. The value-based dimension of a product is when a product provides good value for money. The product-based quality dimension is pertinent to this study in terms of determining if the NAM is fit for its intended purpose.

In addition, and in view of the aforementioned definitions of quality, Garvin (1984 cited in Foster 2012) developed a list of eight quality dimensions, namely:

1. **Performance:** This is the efficiency with which a product achieves its intended purpose. The performance of the NAM in reducing surface roughness will be evaluated in terms of the acceptable threshold value of 0.2µm (Bollen *et al.* 1996; Quirynen *et al.* 1996; Bollen, Lambrechts and Quirynen 1997).

2. **Features:** These are the attributes of a product that supplement the product's basic performance. Here, accurate measurement and characterisation of the particle size of the NAM is significant to the quality of its performance (Basim and Khalili 2015).

3. **Reliability:** This is the propensity of a product to perform consistently over its useful design life. The reliability of the NAM will be assessed by repeatability and reproducibility tests, particularly maintaining a threshold value of 0.2µm in the polishing of the PMMA specimens (Quirynen and Bollen 1995; Al-Kheraif 2014).

4. **Conformance:** When a product is designed certain numeric dimensions for the product's performance need to be established, such as capacity; speed; size; and durability. These numeric product dimensions are referred to as specifications. The conformance of the NAM will be in line with the criteria and standards of the ANSI/ADA specifications for dental abrasive materials, as highlighted in Table 1.

5. **Durability:** This is the degree to which a product tolerates stress or trauma without failing. The durability of the NAM relates to the hardness of its particle size. The tendency of the particles to break down into newly-sharp edges will determine its quality as an abrasive material (Anusavice and Antonson 2013).

6. **Serviceability:** This is generally determined by the ease of repair of a product. With reference to the NAM, serviceability is the extent to which dental technicians can easily manipulate this material during denture fabrication processes, particularly through the use of conventional dental laboratory equipment.

7. **Aesthetics:** These are subjective sensory characteristics such as taste, feel, sound, look, and smell. The aesthetics of the NAM relate to its colour and odour.

8. **Perceived quality:** This is based on the customer's opinion on the quality of a product.

As illustrated in Figure 2-3, and in line with ISO 9001 (2008), a quality process requires the evaluation of information relating to products in terms of whether the product has met its requirement for its intended use. The ISO 9001 (2008) further outlined the methodology known as 'Plan-Do-Check-Act' (PDCA), which is applied to all processes of product development for quality assurance; PDCA is briefly described as follows:

- **Plan:** Are the objectives and processes necessary to deliver results in accordance with customer requirements and the organisation's policies?
- **Do:** Is implementing the processes.
- **Check:** Is to monitor and measure processes and product against policies, objectives and requirements for the product, and to report the results.
- **Act:** Take actions to continually improve process performance.

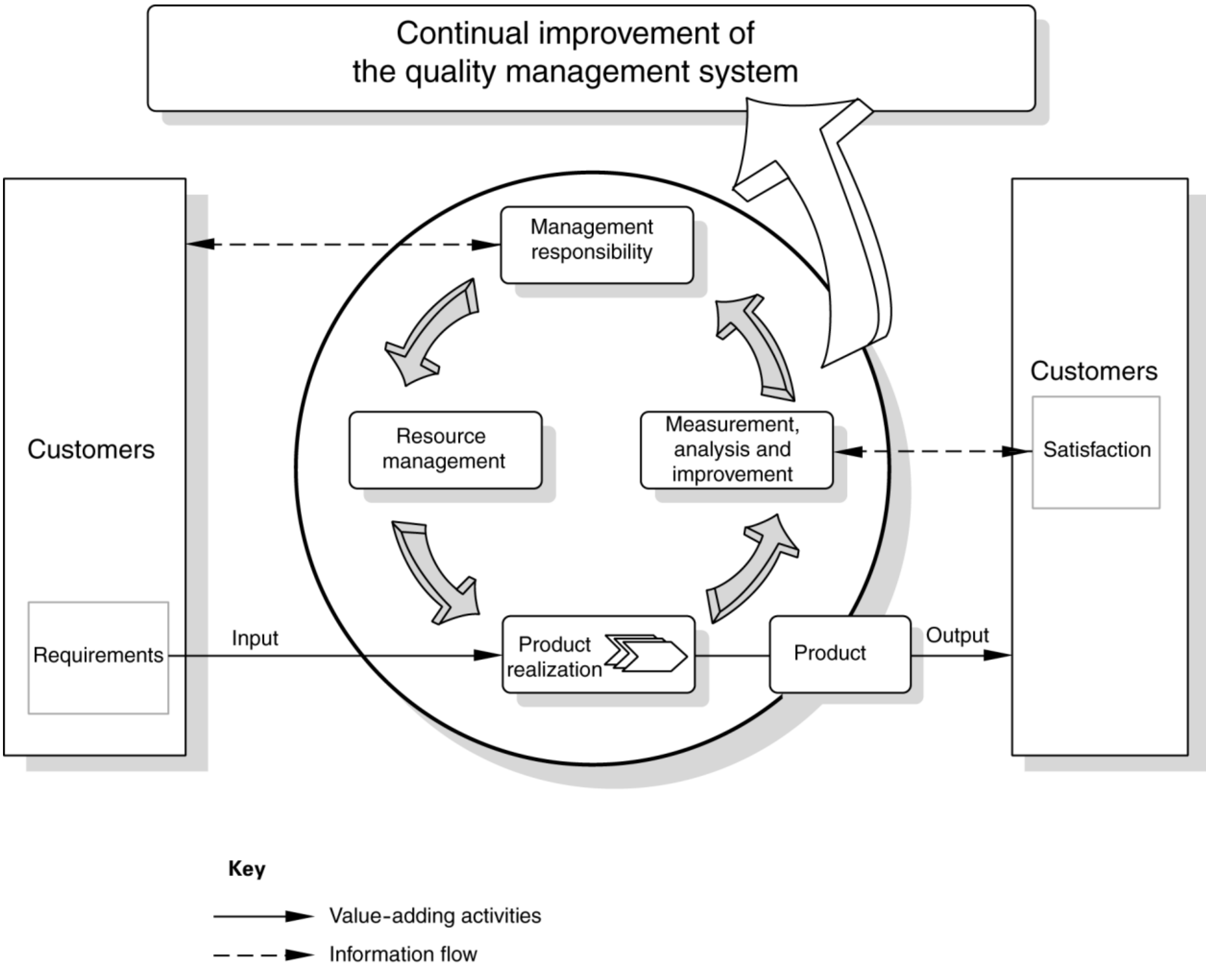


Figure 2-3: Model of a process-based quality management system (adapted from ISO 9001 (2008)).

The above-mentioned criterion of quality is streamlined to add value to the quality management process. Phillips (2013) pointed out that the management process ensures that the quality of the product is achieved the very first time. He asserted that management process gives quality assurance to the product by preventing mistakes, re-work, corrective actions, and a breakdown of the product when used. This is pertinent to this study, particularly in terms of developing a NAM of good quality.

2.8. Impact of cost on the selection of an abrasive material

The selection of an abrasive material is primarily based on two broad objectives: quality and economics. The earlier work of Snyder and Beuthin (1989) contends that the economics of abrasives is determined by its initial cost, as well as the production rate that can be achieved when it is used. Part of the objectives for this study, and as mentioned in Chapter One (Section 1.3.5.1), is to compare the cost of developing the NAM with that of pumice. According to Anusavice and Anthoson (2013: 243) pumice is a type of natural abrasive. Other types of natural abrasive used in dental field include Arkansas stone; calcite; corundum; diamond; emery; garnet; quartz; sand and tripoli. Olson (2001) argued that unlike natural abrasives the improved physical properties associated with manufactured abrasives generally dominate the high-grade abrasive market, which is tailored to meet user needs. Notwithstanding this, he together with Hood (2013) further maintained that the cost is a critical factor when selecting an abrasive material. The cost of using an abrasive material according to Hansink (1998: 25) is mathematically calculated by using the following formula:

Total cost = $\frac{A*(B+C)+D+E}{X} + F$ (per unit/meter square).

Where:

A – Consumption of abrasive of abrasive (kilogram/hour).

B - Cost of abrasive (per unit/time).

C - Cost of storage (per unit/time).

D - Cost of equipment and labour (per unit/hour).

E - Cost of recycling (per unit/hour).

F - Cost of reducing and controlling environmental pollution (per unit).

X - Productivity (meter square/hour).

Hansink (1998) also asserted that in comparing the cost of abrasives, parameters such as test area (m^2); time (min); consumption (kg/hr); efficiency (kh/m^2); cleaning rate (m^2/hr); cost (amount/metric tonne); clean-up ($amount/m^2$) and disposal ($amount/m^2$) of the abrasive usage needs to be considered. His assertion is supported by Strumberger, Maletic and Cvecic (1999) that the amount of abrasive used depends largely on the equipment and the final desired result. Furthermore, and according to Foster (2012: 115), there is a correlation between how a product competes in the market and the cost of the product in industry. Cognisance of this, together with the aforementioned parameters, will be taken into account when comparing the cost of the NAM with that of pumice.

In summary, this chapter outlined the characteristics of abrasive materials in terms of hardness, particle shape and size. These factors are fundamental in the development of a new alternative polishing material. The foregoing reviewed literature further highlighted the microbial considerations in producing an eggshell powder that is free of bacterial contamination. Furthermore, standards for abrasive powders were reviewed as it is an underpinning concept with regards to assessing the quality of a NAM. Overall, the selection of abrasives significantly depends on the product quality and cost of the abrasive material. The next chapter describes the philosophical stance of the research design and methodology adopted in the present study. In particular, the development and testing of the NAM will be discussed in detail.

Chapter Three – Research Design and Methodology

This chapter details the research design and used in this study. The pilot study that was conducted will first be described, particularly highlighting the development of the new abrasive material (NAM) using eggshells. Subsequently, the methodology used in the main study, that is the various experimental work and analyses that were conducted, will be described in-depth.

3.1 Introduction and Background to the research methodology

Generally, research is stimulated by a number of methods such as deductive reasoning, inductive reasoning, the scientific method of enquiry and critical thinking, amongst others (Welman, Kruger and Mitchell 2005; Berg and Latin 2008). Observations and inductive reasoning provided the basis for the initiation of this study. The president of the ADTN (Okeke 2014) observed that the limited supply of pumice prompted dental technicians to re-use pumice slurry in the dental laboratories. This led to an increase in cross contamination in dental laboratories. Okeke (2014) therefore advised that alternative materials to pumice need to be sourced and investigated. Inductive reasoning revealed that the calcium of eggshells provides abrasive characteristics that are similar to pumice (Arias *et al.* 2006; Jayasankar, Mahindran and Ilangovan 2010; Brand-Garnys 2014), thus it could be used as an alternative abrasive material. As this study sought to develop a new abrasive material, a quantitative research design and an experimental research strategy was used. As Johnson and Christensen (2008: 33) explained, a quantitative approach tests "hypotheses with empirical data to see if they are supported". They also maintained that an experimental research strategy enables the researcher to manipulate the independent variable and measure the dependent variable in order to "identify cause-and-effect relationships" (Johnson and Christensen 2008: 33). To facilitate the proposed research design and methodology, a two-phase methodology was deemed appropriate: Phase One – Pilot and Phase Two – Main.

3.2 Pilot Study: Developing and testing of the new abrasive material

As confirmed by several authors (Blanche and Durrheim 2002; Cohen, Manion and Morrison 2007; Johnson and Christensen 2008; Thabane *et al.* 2010; Johnson and Christensen 2012) pilot testing helps to increase the reliability, validity and practicability of the research. Essentially pilot tests sharpen research procedures, clarify the permissions and approvals needed to conduct the study, provide indicative costs in time, and check the feasibility of the larger study.

In developing the NAM, eggshells were first collected from hatcheries and fast food outlets within Durban, South Africa. All preparation and development of the NAM was done at the Mechanical Engineering Material and Strengths Laboratory (Durban University of Technology, Durban, South Africa). The Council for Scientific and Industrial Research (CSIR) Materials Science and Manufacturing department in Pretoria, South Africa assisted in ball milling and characterising the NAM.

As advocated by several authors (Tsai *et al.* 2008; Shuhadah and Supri 2009; Hussein, Salim and Sultan 2011; Bhaumik *et al.* 2012; Hassan and Aigbodion 2013; Oliveira, Benelli and Amante 2013; Brand-Garnys 2014), and in line with the American National Standard Institute/American Dental Association specification no. 37 (American National Standard/American Dental Association 1986: 951-952) standards for dental abrasive powders, the NAM was developed based on the formulae below:

- **Washing and disinfecting of the eggshells:** Eggshells were washed with regular household detergent and subsequently disinfected by storing them for six hours in a diluted solution of household sodium hypochlorite. This facilitated the removal of bacteria such as Salmonella and *E-coli*, which are commonly found on eggshells.

- **Vacuum Drying:** To burn out the membranes the eggshells were vacuum dried for ± 6-9 minutes at 250°C.

- **Grinding:** A motor grinder (Philips HR203®) was used to crush the eggshells into powder (Figure 3-1).

- **Addition of Additives:** Linear alkylbenzene sulfonate (Surfactant; 0.06kg) was added to the eggshell powder (1.26kg) under stirring until homogeneous dispersion was obtained to improve its solubility in water.

- **Ball Milling:** The eggshell powder and surfactant mixture was placed in a 500ml stainless jar (inner diameter of 100mm), together with stainless steel balls (10mm diameter). Subsequently, the mixture was dry-milled in a planetary ball mill (Retsch PM 100®). The grinding operation involved milling for 20 minutes in a clockwise direction, and 20 minutes in an anticlockwise direction. There was a five second interval between the milling. It must be noted that the fine powder obtained in the first milling stage, which used 10mm milling balls, was further ball milled to nano size using 1mm milling balls for 10 minutes (Table 3-1). The NAM was then stored in a sterile container and kept in a cool dry place.

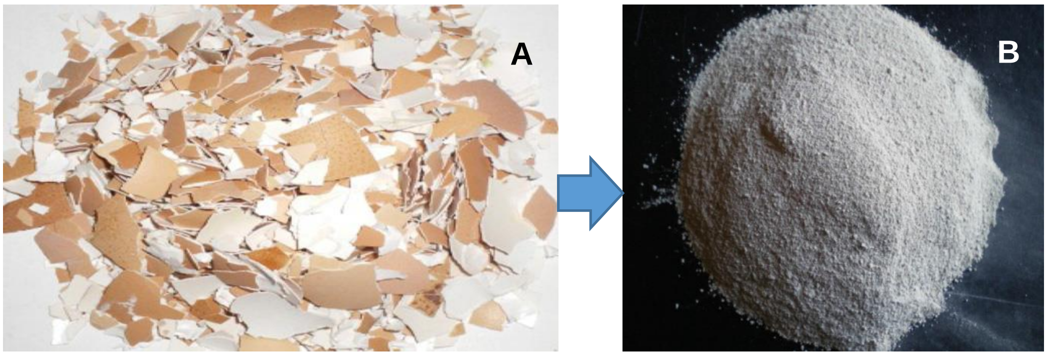


Figure 3-1: Eggshell transformation process: **(A)** Eggshells; **(B)** Eggshell powder.

Table 3-1: Different stages of the Ball milling process.

Duration of Ball Milling (minutes)	Speed (RPM)	Ball mill diameter (mm)
40	400	10
10	400	1

From a quality management and quality assurance perspective, and in line with International Standard Organisation (ISO 9001) (2008) outlined in Chapter Two, the physical characteristics of the NAM were determined in terms of particle size;

crystallinity; hardness; pore volume; surface area of the NAM. These characteristics are described in the sections below.

3.2.1 Mechanical Sieving

As illustrated in Figure 3-2, and following the American Society for Testing and Materials (ASTM C136-06) standard for sieving abrasive size, the NAM was sieved (Labotec sieving mesh, SABS 197-1971) into different particle categories, namely: nano; fine; and medium.

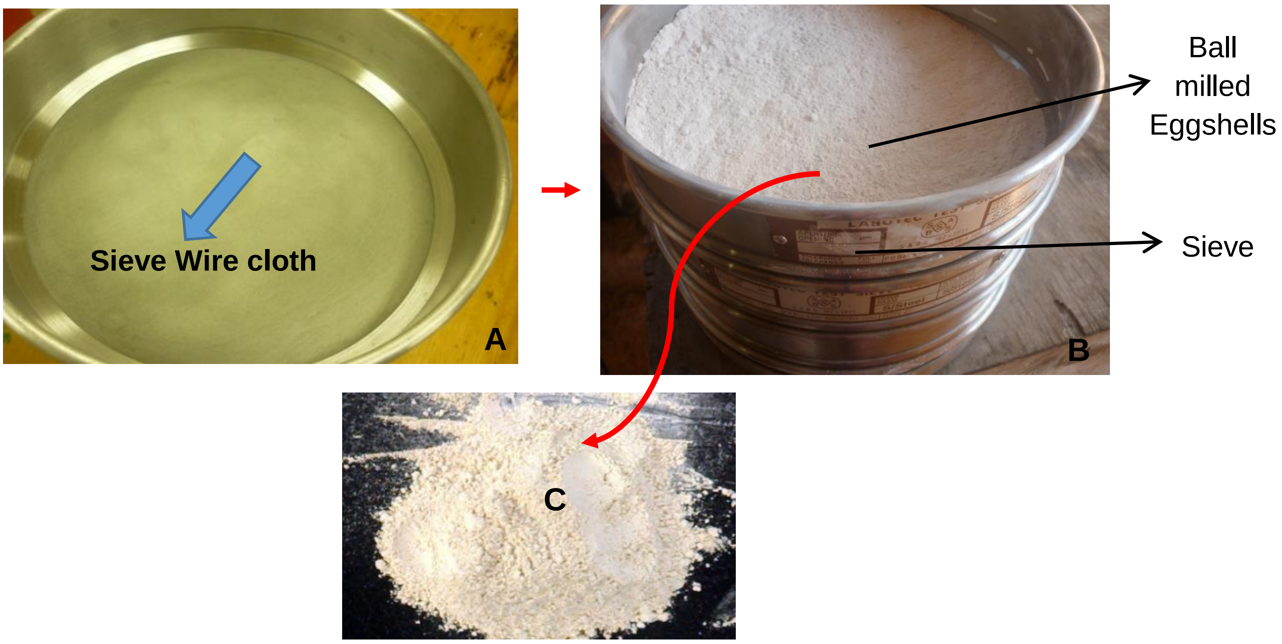


Figure 3-2: Sieving process: **(A)** wire cloth; **(B)** sieving mesh; **(C)** NAM.

3.2.2. Brunnae-Emmet teller (BET) surface area analysis

The surface area, pore volume, and pore size distribution of the NAM from each of the particle categories mentioned above were obtained by measuring the nitrogen adsorption–desorption isotherms at 90° for an hour and 200°overnight. This work was carried out using a surface area and porosity analyzer (Micromeritics Co., USA; Model No.: ASAP 2020). Brunnaer–Emmett–Teller (BET) surface area (SBET, m2/g) and total pore volume (Vt, cm3/g at STP) were thus obtained by the Nitrogen adsorption data. The pore size distribution was calculated based on differential pore volume of Barrett–Joyner–Halenda (BJH) adsorption–desorption.

3.2.3 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) analysis (Perkin Elmer Universal ATR spectrum 100 series) was used to identify the structure and the functional group constituents' parts of NAM. This was to confirm the presence of calcite structure in NAM. A background scan was first performed before analysis of the samples. Subsequently, a small quantity of NAM powder was placed on the sample holder for analysis. It is worth noting that FTIR is an effective analytical instrument that detects functional groups and characterising covalent bonding formation (Simonescu 2012).

3.2.4 X-ray diffraction

The X-ray diffraction (XRD) analysis was performed to observe the possible changes in crystallinity and mineral content of the NAM. The XRD patterns were recorded using a diffractometer Empyrean (PANalytical instrument; Co- radiation 1.54056 A°) and analysed between 10-80° (2 theta). The voltage, current and pass time used were 40 kV, 40 mA and 1s, respectively. According to Dutrow and Clark (2008), XRD is most widely used method for identification of unknown crystalline materials and their mineralogical composition.

3.2.5 Laser Scattering Particle Size Distribution Analyser

The particle size distribution of the NAM was measured using a HORIBA Laser Scattering Particle Size Analyser (PSA: LA-950). The NAM powders were dispersed in Isopropanol and used in the funnel of the Analyser LA-950. The form of distribution was set at manual mode. Particle size distribution was calculated on the volume basis. Refractory index of NAM and Isopropanol were kept at 1.660-1.378, respectively. Brummer (2008) and Basim and Khalili (2015) noted that the PSA is highly suitable for accurate determination of particles in a range of 0.02µm to 2000µm. In light of their report, PSA technique was used in this study to ensure accurate measurement, reliability and reproducibility of the particle size distributions of NAM.

3.2.6 Energy Dispersive X-ray Spectroscopy and Scanning Electron Microscope analysis

To analyse the elemental composition and to characterise the surface morphology of the NAM, an energy dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM: S-3000N-Carl Zeiss) that operated under controlled atmospheric conditions at 120 kV were used, respectively. EDX technique detects X-rays emitted from the sample during bombardment by an electron beam. The EDX X-ray detector measured the relative abundance of emitted X-rays versus their energy. The SEM analysis was performed to show the morphology of the particle sizes. Prior to SEM observations, the surface of the sample was coated with a thin, electric conductive gold film to prevent the accumulation of electrostatic charge.

3.2.7 Transmission electron microscope

As reported by Howe, Fultz and Miao (2012), Transmission Electron Microscope (TEM) is the foremost instrument for understanding the internal microstructure of materials at the nanometer level. In this study, TEM was used to observe the particle size, shape and distribution of NAM. A very small quantity of NAM powder (three inch of a spatula) was dispersed in 10ml ethanol and sonicated at 10kV for 10 minutes. Subsequently, thin cross-sections of cryo-microtomed specimens were prepared using a Leica microtome (South Africa) and placed on carbon copper grids. Analysis was done using a transmission electron microscope (TEM -Philips CM 120 model) at 120 kV.

3.2.8 Hardness (Scratch) Test

As per Figure 3-3, four different scratch tests based upon the Moh’s hardness test described in Chapter Two were used on the dry eggshells. This included using a fingernail (Mohs hardness value of 2.5); PMMA resin (Mohs hardness value of 2-3); copper penny (Mohs hardness value of 3); and a piece of glass (Mohs hardness value of 5.5). Scratching involved pressing firmly into, and across, the surface of the eggshells.

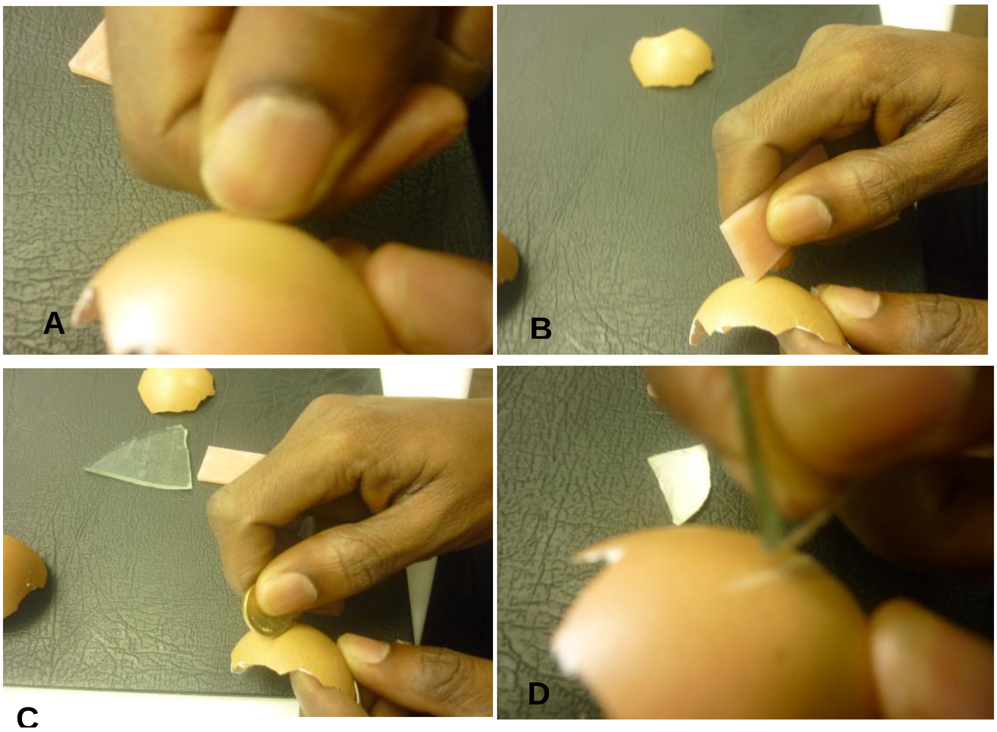


Figure 3-3: Scratch test using: **(A)** fingernail; **(B)** PMMA resin; **(C)** copper penny; **(D)** glass.

3.2.9 Thermo-gravimetric Analysis

Thermal degradation and stability of the NAM was examined using a Thermo-gravimetric analysis (TGA). The thermal stability was measured using a TA instrument (Thermal Universal Analyser V4.5A). The test was performed under a dry nitrogen gas flow at the rate of 100mL/min from 20ºC at a heating run of 10ºC/min. According to the earlier work of Sauerbrunn and Gill (1994), TGA measurement shows evidence about the kinetics of material decomposition, which can be used to predict the in-use lifetime of the material.

3.2.10 Chemical Analysis of NAM

Chemical analyses were performed to ensure that the NAM was free of hazardous substances. This was done in line with the International Standard Organisation (ISO 9001: 2008).

3.2.10.1 Inducting Coupling Plasma (ICP) – Optical Emission Spectroscopy (OES)

As specified by the Chinese Medicine Board (2004) for product safety technical guidelines, ICP-OES methods were used to quantitatively determine the presence of toxic elements. It must be noted that ICP-OES is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths that are characteristic of a particular element. The ICP- OES uses a flame technique with a flame temperature within a range of 5727^{o}C to 972 7^{o}C. After hot plate acid digestion, three different concentrations of the NAM were used (0.1203g, 0.1143g, and 0.1074g) to be analysed for metal ions. This entailed using 10mls of 6M HCl to digest the sample during heating and stirring. The sample was then filtered into a 100ml volumetric flask and topped up with distilled water. The sample was then filtered using a 0.45 micro-filter into an ICP vial. Analysis was performed at a standard range of 2-10ppm.

3.2.10.2 High Performance Liquid Chromatography (HPLC)

It is worth mentioning that Linear Alkylbenzene Sulfonate (LAS), which is readily biodegradable and non-toxic to humans is widely used in laundry detergent formulation and household cleaning products (Akyuz and Roberts 2002; Okada *et al*. 2013). From an environmental perspective, the earlier report of Davies (1992) indicated that LAS concentration of 30-300mg/l inhibit the growth of algae.

Following ISO Horizontal 13.0 (2001), HPLC was used for quantification and identification of Linear Alkylbenzene Sulfonate (LAS) concentration of the NAM. This involved dissolving 0.01g of the NAM into 50ml acetonitrile/water to produce a 200ppm solution. Thereafter, a 20ppm solution was prepared by diluting 0.2ml from the first concentration in 2ml volumetric flask. The HPLC method was based on reversed-phase separation with acetonitrile/water and the phase modifier contained NH_4ClO_4 and TFA. The chromatograph column was set at 4.6mm x 25cm. The pressure was at 350 bars with a flow rate of 1ml/min.

3.2.11 Microbial Analysis of NAM

In accordance with ISO standards (ISO 21149 and ISO 16212) for microbiological control of cosmetic products, microbial analyses were conducted to ensure that the NAM was free from *Salmonella* and *E-coli.* In determining the total number of heterotrophic bacteria, Nurient agar (NA-Biolab) was prepared by adding 32g Nutrient agar powder in 1L water, followed by autoclaving. Once cooled (50°C) agar was then poured into 90mm Petri plates and allowed to solidify. In order to determine the total number of fungi, Potato Dextrose Agar (PDA-Biolab) was prepared by adding 39g PDA agar powder in 1L water followed by autoclaving. Once cooled to around 50°C the agar was poured into 90mm petri plates and allowed to solidify.

A stock suspension of the NAM was prepared by adding 1g of powder to 10ml sterile water. This was vigorously mixed in order to dislodge bacteria, fungi and fungal spores. A serial dilution of the sample was prepared by transferring 1ml of suspension to 9ml of sterile water and this was repeated until a final concentration of 0.01mg/ml was obtained. The suspension concentrations were therefore: 100mg/ml; 10mg/ml; 1mg/ml; 0.1mg/ml; and 0.01mg/ml.

One hundred microliters of the individual prepared dilutions were spread onto six NA and six PDA plates. Three of the NA plates were incubated at 30°C and three incubated at 37°C. Similarly, three of the PDA plates were incubated at 30°C and three incubated at 37°C.

As advocated by Yousef and Carlstrom (2003), the following equation was used to determine the colony forming units/ml of sample:

CFU/ml=number of colonies X dilution factor X 10

3.2.12 Particle size comparison between NAM and Pumice

As showed in Table 3-2, the particle size distribution of the NAM was compared and evaluated. This was achieved by using ASTM, FEPA and ANSI/ADA standards against the particle grades of pumice produced by Hess and Navajo pumice suppliers.

Table 3-2: Specification for particle size distribution ASTM, FEPA and ANSI/ADA standard.

Particle size category	NAM	Brand of pumice		Standards		
		Hess	Navajo	ASTM C136	ANSI/ADA specification 37	FEPA
Coarse	Not Assigned	100-900µm	100-800µm	500-1190µm	100-500µm	1000-1410µm
Medium	45µm	45µm	40-75µm	150-400µm	10-100µm	300-400µm
Fine	0.3µm	21µm	5-8µm	45-180µm	0-10µm	300-400µm
Very fine	Not Assigned	2-4µm	Not Assigned	8-47µm	Not Assigned	3-4µm
Nano-size	50nm	Not Assigned	Not Assigned	Not Assigned	Not Assigned	Not Assigned

3.2.13 Assessing the Abrasivitiy of NAM

3.2.13.1 Preparation of PMMA Specimens

Following ISO 20795-1 (2013), five rectangular steel disk-shaped dies (Figure 3-4) with dimensions of 50mm x 20mm x 3mm were fabricated. The stainless-steel dies ensured that a consistent mould was produced during the 'flasking and packing' procedures. Rawls (2013: 476-478) defined flasking as the process of covering a wax-up pattern in a flask (Figure 3-5), which is subsequently enclosed in a gypsum investing material before processing. Packing, by contrast, involves the placement of heat cure resin material into the mould cavity (Figure 3-6).

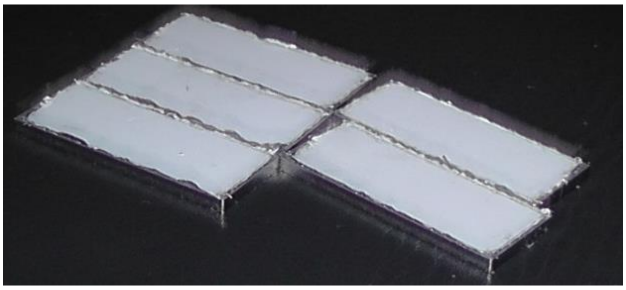


Figure 3-4: Stainless steel dies.

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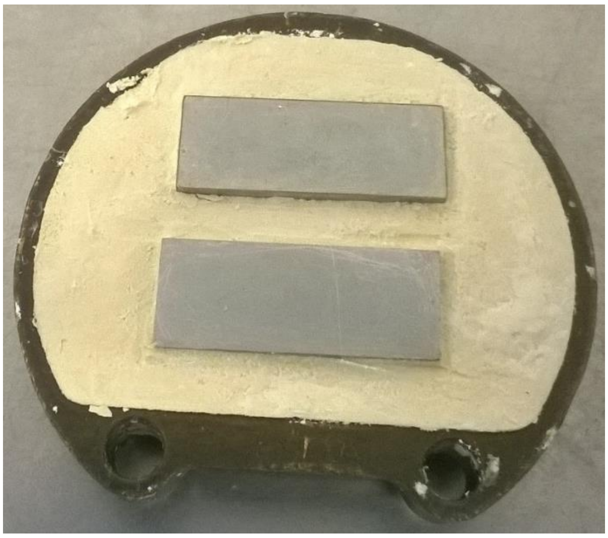


Figure 3-5: Flasking process.

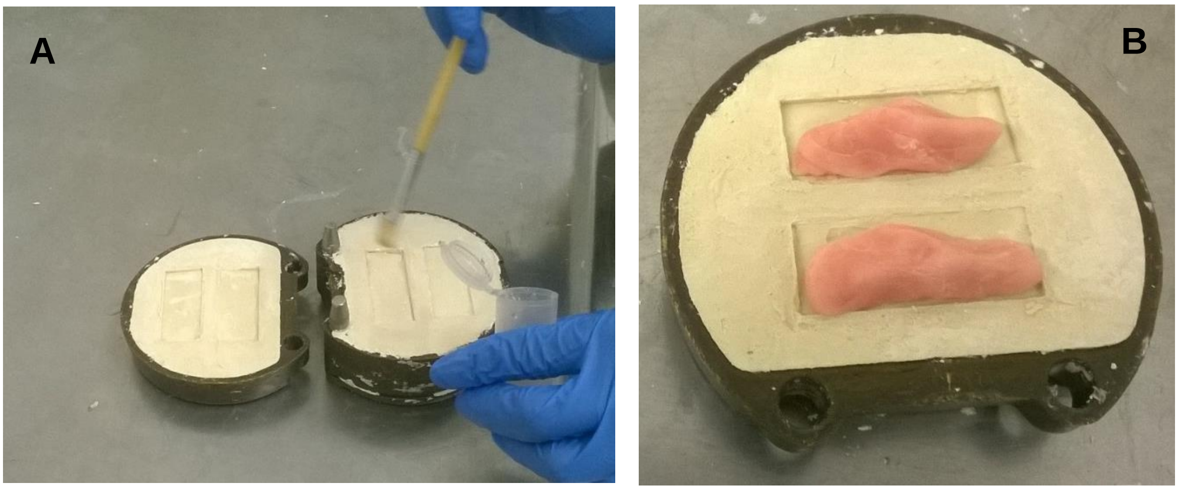


Figure 3-6: Packing process: **(A)** prepared mould; **(B)** PMMA dough in mould cavity.

Prior to packing the PMMA resin dough into the mould, cold mould seal (Wright Health Group Ltd, Dundee, Scotland) was applied. According to Rawls (2013: 476), cold mould seal prevents water absorption from the dental plaster into the PMMA resin dough during processing procedures. This prevents any adverse reactions to the polymerisation rate and ultimately the colour of the resin. Forty-eight PMMA resin specimens were fabricated with heat-cured acrylic resins (Vertex-Dental B.V, Netherlands®). All specimens were flasked and packed as follows:

Following manufacturer's instructions, a polymer/monomer ratio of 30g/10ml was used to form a resin dough, which was hand-mixed with a spatula for 30 seconds in a mixing bowl. Once the mixture reached the dough stage (15 minutes), it was then kneaded and placed into the mould. From Figure 3-7, the flasks were clamped in a bench press using slow pressure, which ensured the even flow of the resin dough within the mould. Curing of the flasks in a water bath then followed. After the curing cycle (Figure 3-8), and following the manufacturer's instructions, the flasks were bench cooled for ten minutes prior to immersing in cool water.

Figure 3-7: Bench press.

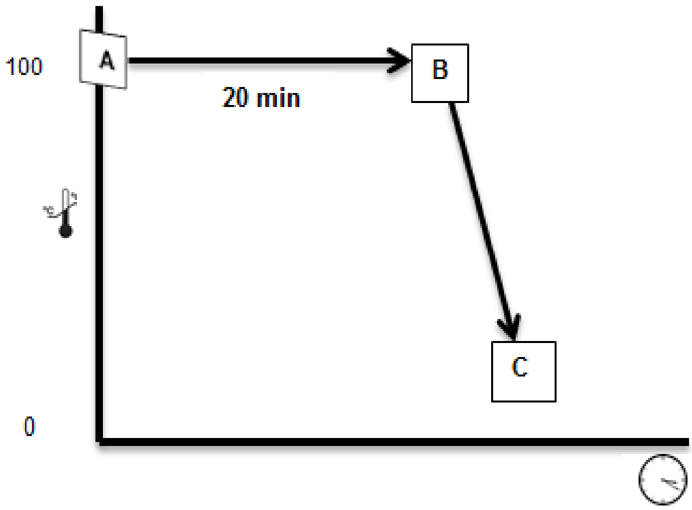


Figure 3-8: Curing cycle **(A)** Start curing process in hot water + Maintain water temperature **(B)** Stop curing + Air cooling to ambient temperature **(C)** End total curing process.

3.2.13.2. Conventional Hand Polishing of PMMA Specimens

The PMMA specimens were trimmed with a tungsten carbide bur (Cross-cut, coarse - ISO No. 500104237065, Bredent GmbH & Co KG) at 18,000 rpm for 1 minute and 30 seconds. An abrasive paper (CC768 Silicon Carbide, Deer Abrasives, Ridgefield, NJ, USA) was used to smoothen all the specimens. The PMMA specimens were then polished using different particle sizes of the NAM (Table 3-3), in order to determine the particle size that produces the most effective surface finish. As advised by Julious (2005) a sample size of twelve per sample group is deemed appropriate. Consistency of the slurry was achieved by mixing 30g of the NAM with 5ml of distilled water. All finishing and polishing was done by one operator to reduce variability in the polishing process. All specimens were hand polished on a laboratory lathe machine (Figure 3-9). Polishing was performed at a revolution of 1500 rpm at an interval of one and two minutes, respectively.

As Corsalini *et al.* (2009) noted, surface roughness of PMMA resins is affected by the inherent features of the abrasive material, polishing technique and the operator's manual skills. Although ISO 20795-1 (2013) regulates the first two factors, namely material characteristics and polishing techniques, the standard does not provide any details with regard to the operator's skills. In attempting to address this, two different operators were used to hand polish the PMMA specimens for two minutes in order to ascertain levels of consistencies in the polishing procedures. As shown in Addendum 6, statistical differences were found in the R_a values between different operators. Hence, automatic polishing procedures were used in the main study.

Table 3-3: Different particle sizes of the NAM.

NAM Sample Group	Particle size	Number of Specimens	Speed (RPM)
Nano-size	50nm	12	1500
Fine	≤ 0.3 µm	12	1500
Medium	≥ 45 µm	12	1500

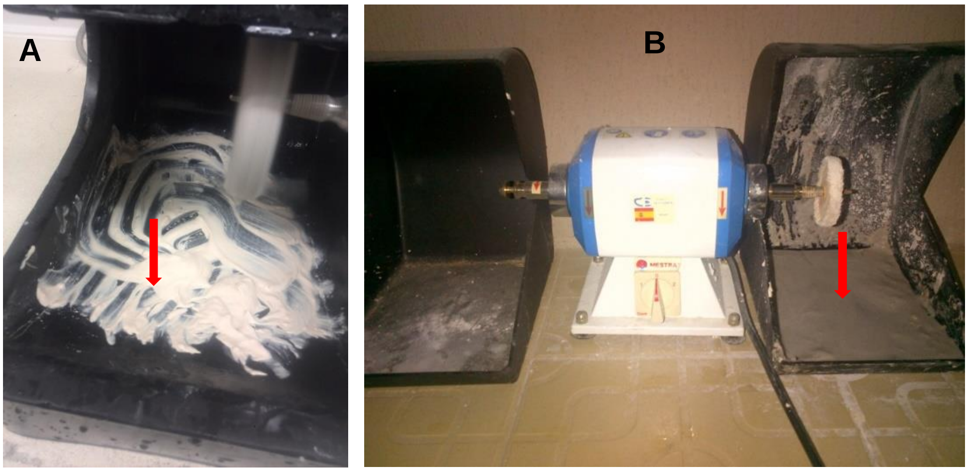


Figure 3-9: Conventional polishing lathe machine: **(A)** NAM slurry in a trough; **(B)** pumice slurry in a trough.

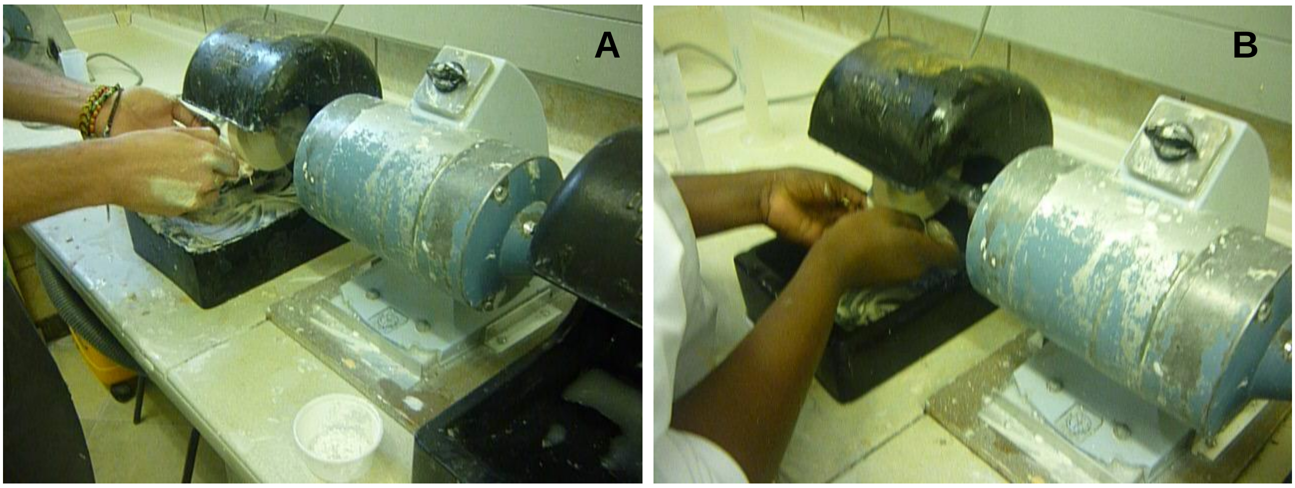


Figure 3-10: Conventional hand polishing: **(A)** Operator 1 and **(B)** Operator 2.

3.2.13.3. Surface analysis of polished PMMA specimens

The surface roughness (R_a values) of the PMMA specimens were analysed using a Wintrace surface analysis system (Taylor Hobson®). The profilometer was calibrated with a cut-off filter 0.8mm, together with an evaluation length of 4.00mm and a range of 5.1µm. Five R_a value measurements of surface roughness were performed for each specimen, and the mean average was used for the statistical analysis.

In addition, qualified dental technicians (n=8) were purposively selected from the Dental Sciences Department at the DUT, to further validate the NAM by assessing the surface smoothness of the PMMA specimens at first glance. The small number of qualified dental technicians in the Dental Science Department, DUT, supported census sampling (Check and Schutt 2012: 96). As shown in Addenda 1 and 2, ethical clearance and permission to conduct the study was obtained from the Research Higher Degrees Committee (RHDC) of the Faculty of Health Sciences at the DUT, and the Institutional Research Ethics Committee (IREC), respectively. Written consent was obtained from each participant**,** who were assured anonymity (Addendum 3). Participants used a rating sheet to record their assessment of the PMMA specimens (Addendum 4).

Figure 3-11: Polished PMMA specimens.

3.2.13.4. Statistical analysis

Using SPSS (Version 23®)), a Shapiro-Wilk test was used to determine the normality of the R_a values. One-way analysis of variance (ANOVA) was used to compare the polished surfaces of the PMMA specimens. The ANOVA parametric tests can be used to identify the mean differences and for testing any significant differences of more than two variables (Cunningham and Aldrich 2012). Tukey and a Bonferroni tests were also done to determine any significant differences in the polished PMMA specimens by the two different operators. The level of significance used to determine the mean differences was 0.05. Using Microsoft Excel (Version 2013®), the participants' assessments of the polished PMMA specimens were analysed. The results of their ratings are presented in bar graphs (Addendum 5).

3.2.14 Cost comparison of the NAM and Pumice

The total estimated cost for the NAM and Pumice were calculated as follows:

- The PMMA test areas were measured in accordance with the rectangular steel disk dies (Figure 3-4).
- Time for polished was set at two-minute intervals for all samples.
- Prior to polishing, dry powder NAM and pumice used were measured. Post polishing, the used NAM and pumice were measured to determine the consumption rate.
- The efficiency of the NAM by comparison with pumice was calculated using the formulae F/E x 100, where:

  F- Number of sample polished x Standard allowed minutes for polishing.

  E- Number of operator x Working hours x 60.

- Production costs were calculated based on the estimated cost of the surfactant additives, which was R28.45. Addendum 5 shows the production cost estimate for pumice that is R157.68.
- Finally, the total estimated cost for the NAM and Pumice was calculated as follows:

Total cost = Consumption x Cost of abrasive/Efficiency.
(Hansink 1998).

3.2.15 Overview of the pilot study

This section summarises the findings of the pilot work.

- No statistical differences were found between the PMMA specimens polished at one and two minute intervals. In spite of this, the lowest R_a value was obtained at two minutes (Addendum 6). Hence, this time was selected for the main study.

- The fine particle size of the NAM revealed the lowest R_a value. This particle size was used to polish the PMMA specimens for the main study. This was further verified by qualified dental technicians who assessed the PMMA specimens (Addendum 6).
- To minimise differences in R_a values recorded between different operators, automatic polishing procedures were used in the main study. This helped to maintain uniformity and consistency in the polishing of the PMMA specimens.

3.2 Main Study: To establish the product-based quality of NAM in terms of 'fitness for purpose'

3.3.1 Sample Size and Preparation of Samples

Somekh and Lewin (2011: 223-224) advised that 30 specimens should be used in experiments where comparisons between two or more groups are made. In line with their advice, and using the rectangular steel disk-shaped dies (Figure 3-4), 100 PMMA specimens were fabricated. The stainless-steel dies were used to ensure a consistent mould was produced during 'flasking and packing' procedures. All sample preparation followed the procedure as outlined in section 3.2.13.1. There were two sample groups of fifty specimens in each group (n=100). Fifty specimens were polished with the NAM and the other fifty with pumice.

3.3.2 Mechanical Polishing of the PMMA Specimens

Prior to polishing, the specimens were embedded in a mounting resin (AMT Composite^{TM}). The embedding preparation was conducted as follows:

I. A silicon mould was used as the mounting base for the composite (Figure 3-12).
II. PMMA specimens with dimensions of 15mm x 15mm x 3mm were fitted into the mould.
III. The fast setting resin was prepared in a disposable plastic cup by mixing the part A and part B (Composite^{TM}) in the ratio 1:1, which was subsequently poured into the mould.

IV. After ±2 minutes the embedded resin was removed from the silicon mould.

V. Grinding of the embedded PMMA specimens was done using silicon carbide papers (CC768 Silicon Carbide, Deer Abrasives, Ridgefield, NJ, USA).

VI. Automatic polishing of the PMMA specimens then followed. This involved using a milling tool as a mobile support for the PMMA specimens and a micrometric advanced isoparallelometer to polish. An equal volumes of the NAM and Navajo® pumice (4-8µm) that is 60mg was mixed with 50ml distilled water. The weight of the polishing material was controlled by using an electronic measuring balance and the quantity of distilled water controlled by using a hypodermic syringe. As illustrated in Figure 3-13, automatic polishing was performed for two minutes, under 300 rpm and 500g of load (Struers Rotopol-35, Pdm force-20).

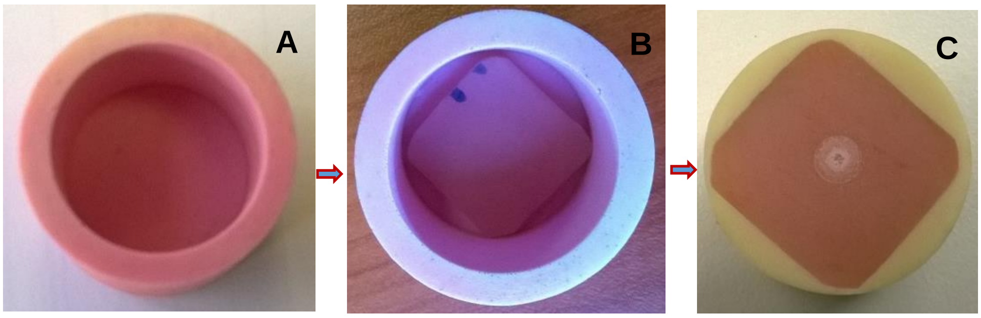


Figure 3-12: The embedding process: **(A)** Silicon mould; (**B**) PMMA fitted to the mould; (**C**) PMMA embedded in a resin**.**

Figure 3-13: (A) Schematic of the mechanised polishing units; **(B)** Polished PMMA resin.

3.3.3 Sample Testing and Analysis

As mentioned in Chapter Two, to fully characterise the quality of surface finish of the polished PMMA specimens different surface measurements were used.

3.3.3.1 Surface roughness analysis

The surface roughness (R_a values) of the PMMA specimens was analysed using a Wintrace surface analysis system (Taylor Hobson®). The roughness parameter R_a was measured and subsequently used for statistical analysis. As highlighted in the ISO 4287 (1997) standard, R_a corresponds to the average peak and valley distance. A point deserving of mention is that the profilometry calibration and measurement (Figure 3-14) follows the procedure as outlined in Section 3.2.13.3.

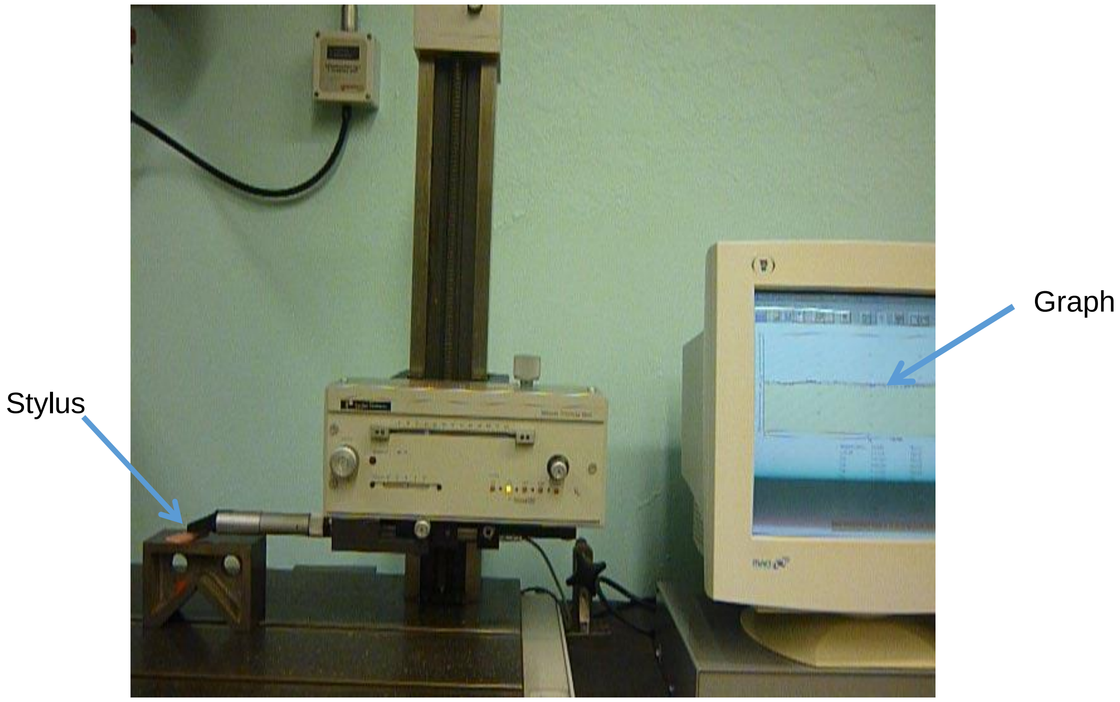


Figure 3-14: Profilometry analyses of the PMMA specimens**.**

3.3.3.2 Scanning electron microscope and Optical electron microscope observation

In characterising the surface morphology of the polished PMMA resins, one specimen from each of the sample groups, namely the NAM and pumice, were analysed microscopically using a Scanning electron microscope (Carl Zeiss®) and an optical electron microscope (Optimus Bx45). As a proxy measure, the surface morphology of the specimens polished with the NAM and pumice were compared against an unpolished PMMA specimen. This was to determine the reduction of surface roughness at each processing stage, being grinding, smoothening, and polishing.

3.3.4 Data analysis

Statistics has two broad genres namely, descriptive and inferential. Lind, Mason and Marchal (2002) elaborated that descriptive statistics describe, organise and summarise a particular set of quantitative data. Although such statistics makes no inference or predictions they are, however, useful in summarising results for an experiment. Both Univariate and Bivariate descriptive statistical procedures were used to analyse the data in this study. Salkied (2007) and Field (2009) pointed out that Univariate and Bivariate is most appropriate for descriptive statistics. Bar graphs and tables were used to present the data. Non-parametric test using Kolmogorov-Smirnov (KS) test was used to determine the normal distribution of the R_a values. Kinnear and Gray (2004) and Cunningham and Aldrich (2012) asserted that the purpose of KS is to determine if the distribution of values approximates the normal curve.

With reference to the inferential statistical analysis, Johnson and Christensen (2012) explained that inferential statistics, by contrast, uses the laws of probability to make inferences and draw statistical conclusions about the sample data. Basically, inferential statistical tests are used to examine the hypothesis in a study (Creswell 2009). In testing the hypothesis for this study (Chapter One, Section 1.4), Barnes (2011) indicated that the independent t-test is the most appropriate parametric test to identify the mean differences, and for testing any significant differences between two variables. The independent t-test was used to analyse the R_a values between the PMMA specimens polished with the NAM and pumice, with $p<0.05$ set as statistically significant. All analyses were performed using SPSS (Version 23®).

3.3.5 Validity and Reliability

Criterion validity, which is premised on internal validity, was used to ensure the accuracy of the data analysed. As pointed out by Leedy and Ormrod (2005), internal validity allows accurate conclusions about cause and effect relationships within the data. In terms of validity for this study, the ISO 20795-1 (2013) guidelines were followed for the preparation, fabrication and testing of the PMMA specimens. The validity and reliability status of instruments and equipment have been included in Addendum 8 on page 104.

With reference to reliability, Walker (2011) pointed out that the reliability of an experimental procedure is determined via reproducibility and repeatability tests. As explained by Slezák and Waczulíková (2011) and Vitek and Kalibera (2011), reproducibility is the variability of the average values obtained by several observers while measuring the same item. On the other hand, repeatability is the variability of the measurement obtained by one person while measuring the same item repeatedly. In terms of the reproducibility in this study, different dental technicians were used to polish the PMMA specimens. In addition, the similarity in the average R_a value measured by the number of times the polishing processes were repeated confirmed the repeatability of the test.

Overall, this chapter detailed the research paradigm and the experimental procedures undertaken in the study. The subsequent chapters will provide a rigorous discussion on the study results and will consider future directions for this research.

Chapter Four – Results and Discussion

This chapter presents the results and discussions of the pilot and main phases of this study. The data collected for both phases were analysed in relation to the research objectives as outlined in Chapter One, that is: to develop a New Abrasive Material (NAM); and to establish the product-based quality of the NAM in terms of 'fitness for purpose'.

In phase one the first six research objectives were addressed. Here, the physical characterisation of the NAM in terms of its crystallinity; hardness; pore volume; particle size and surface area were established. The thermal stability and degradation of the NAM, the degree of bacterial contamination and the different metal ions present in the NAM were conducted. By comparison with pumice, the production cost of developing the NAM and using different abrasive standards such as American Standards/American Dental Association (ANSI/ADA) and the American Society for Testing and Materials (ASTM) were also investigated. In phase two, the research hypothesis outlined in Chapter One, Section 1.4, was explained in terms of assessing the suitability of the NAM as an alternative material to pumice. In particular, a profilometer was used to measure the surface roughness of the PMMA specimens polished with the NAM. Scanning Electron Microscopy (SEM) was used to examine the surface characteristics of PMMA specimens polished with the NAM. Both the profilometer and SEM results of the NAM were compared with the results obtained from pumice. Apart from the characterisation data, all other data were statistically analysed in order to ascertain the quality of the NAM as an alternative abrasive material. This chapter concludes with a summary of the data that was analysed.

4.1 Phase One – Pilot Study

It must be noted that eggshell powder without additives was used as a point of reference when discussing the structural changes of the NAM.

4.1.1 Physical characterisation of the NAM

As shown in Table 4-1 the pore size of eggshell powder is 279nm, which is directly proportional to its small BET surface area (0.0362 m^2/g). The NAM which was ball milled to nano, fine and medium sizes revealed 13, 16 and 14 pore sizes, respectively. It must be noted that porous materials are classified as microporous, mesoporous and macroporous. As highlighted in the IUPAC notation (Rouquerol *et al.* 1994; Zdravkov *et al.* 2007), microporous materials have pore diameters less than 2nm, whereas macroporous materials have pore diameters greater than 50nm. The mesoporous category hinges between the aforementioned diameters. From the results in Table 4-1, it can be gathered that the NAM is typically a mesoporous material. This finding is consistent to the earlier work of Filio *et al.* (1994), in that the mechanochemical effects associated from ball milling granular material causes a reduction in particle size and changes to the microstructure overall. The BET results further suggest that the abrasive characteristics of the NAM are similar to pumice (Chapter 2, Section 2.1).

As highlighted in Figure 3.3 in Chapter Three, the various hardness tests used revealed that the fingernail, copper penny, and PMMA resin did not leave any significant scratches on the surface of eggshell. The piece of glass however, showed an observable scratch on the surface of the eggshell with a Mohs hardness value of 5.5. It can therefore be inferred that the hardness value of eggshell is between 4 – 4.5 as it was harder than the fingernail (Mohs hardness value of 2.5), PMMA resin (Mohs hardness value of 2-3) and copper penny (Mohs hardness value of 3). The hardness value further suggests that the surface roughness will be effectively reduced as it is further than the Mohs hardness value of denture base resin, which is 3. This is consistent with Anusavice and Antonson (2013), that the farther apart the hardness values between the abrasive (NAM) and substrate (denture base resin) then the higher the abrasion.

Table 4-1: BET surface characterisation of Eggshell Powder and NAM.

Materials	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Eggshell powder	0.0362	279	0.002527
NAM-nano	2.3598	13	0.010676
NAM-fine	1.5296	16	0.007862
NAM-medium	1.0656	14	0.004957

4.1.2 Structure, Crystallinity and Mineral Content in NAM

As illustrated in Figure 4-1, the FT-IR spectra for eggshell powder and the NAM measured with several bands from 4000 cm^{-1} to 380 cm^{-1}.

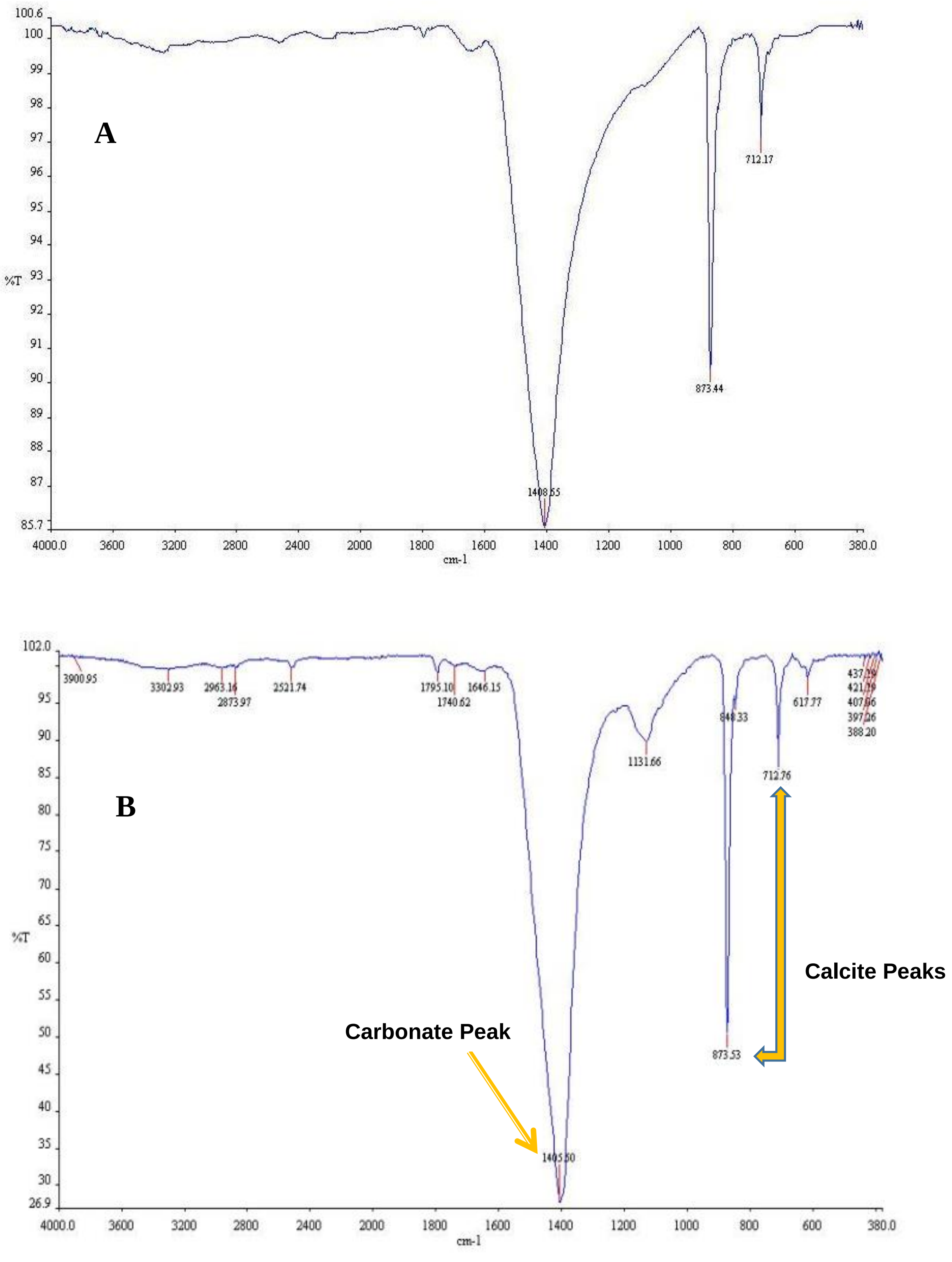


Figure 4-1: FT-IR Spectra - **(A)** eggshell powder; **(B)** NAM.

A prominent absorption peak of carbonates was observed at 1405.50 cm^{-1}, which is associated with the carbonyl group. Carbonate based materials are commonly detected by the broad stretching frequency of the C=O in carbonates ions around 1416 cm^{-1} (Mosaddegh and Hassankhani (2013). Furthermore, the FT-IR graph shows the absorption peak of calcite at 712.76 cm^{-1} and 873.53 cm^{-1}. These were attributed to asymmetric and symmetric stretching, out-of-plane bending and in-plane bending vibration modes for calcium carbonate (CO_3^{2-}) molecules. This supports the work of several authors (Tsai *et al.* 2006; Yao *et al.* 2013; Feng *et al.* 2014; Bashir and Manusamy 2015), where the absorption peak of calcite was reported to be between 712 cm^{-1} and 876 cm^{-1} of CO_3^{2-}. It can therefore be inferred that the ball milling process does not negatively impact on the carbonate structure of the NAM.

From Figure 4-2, the XRD pattern of eggshell powder and the NAM had characteristic diffraction angles at 27.5°, 34.5°, 42.5°, 46.5°, 50.5°, 56°, 57°, 67°, 68°, and 72°. The characteristic peak around 34.5° (2*θ*) indicates that both eggshell powder and the NAM contain a thermodynamically stable calcite crystalline structure. This crystalline structure is similar to the crystalline structure of calcium carbonates as reported by Murakami *et al.* (2007) and Mosaddegh and Hassankhani (2013).

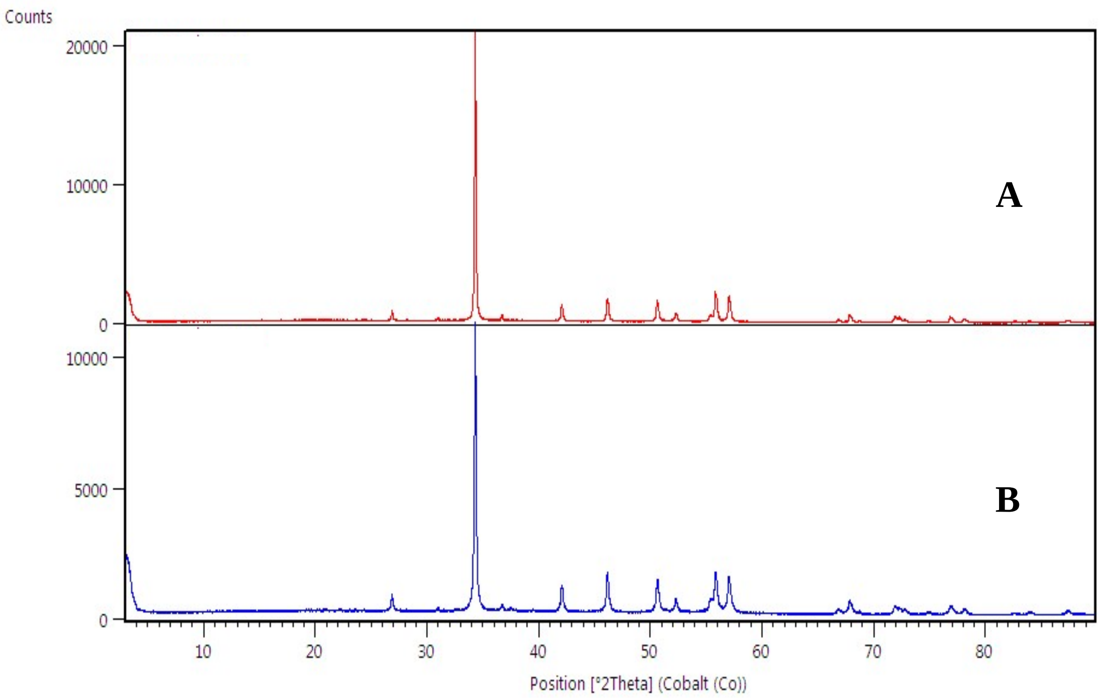


Figure 4-2: XRD pattern showing crystallinity of: **(A)** eggshell powder and **(B)** NAM.

The XRD pattern shown in Figure 4-3 revealed differences in the mineral content of eggshell powder and the NAM.

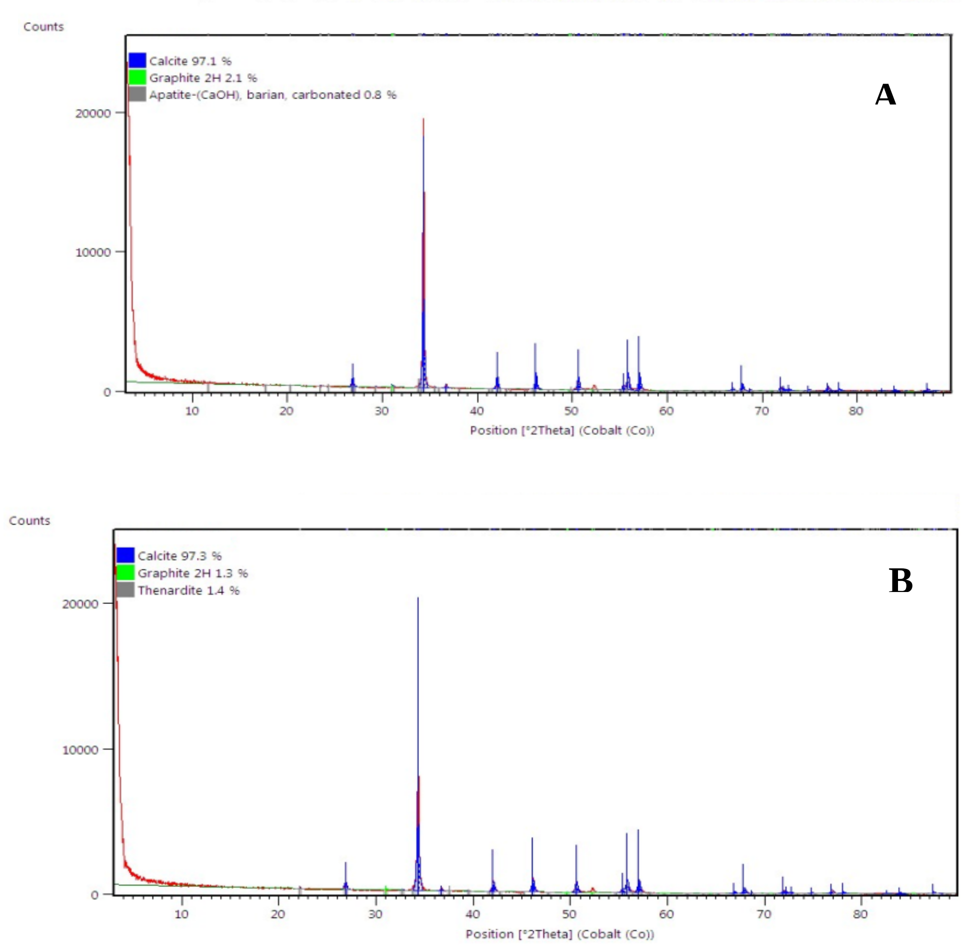


Figure 4-3: XRD pattern showing mineral content of: **(A)** eggshell powder **(B)** NAM.

Table 4-2 shows that eggshell powder and the NAM have different mineralogical compositions. It is worth noting that during crushing of the eggshells into powder, apatite was formed by the interaction of calcium carbonate and moisture (H_2O). This finding corroborates with Oliveira, Benelli and Amante (2013), that calcium hydroxide (apatite) is formed as shown by the chemical equations below:

[1] $CaCO_3 \rightarrow CaO + CO_2$

[2] $CaO + H_2O \rightarrow Ca(OH)_2$

[1] Calcium Carbonate ($CaCO_3$) decomposes into calcium oxide and carbon dioxide.
[2] Calcium oxide and water reacts to form calcium hydroxide, also known as apatite.

Table 4-2: Mineralogical composition of eggshell powder and NAM as determined by XRD analysis.

Mineral	Chemical formula	Eggshell powder	NAM
Calcite	$CaCO_3$	97.1% *(Ref. Code 98-004-0543)*[3]	97.3% *(Ref code.98-007-9674)*
Apatite	$Ca(OH)_2$	0.8% *(Ref code 98-015-1680)*	Absent
Graphite 2H	C	2.1% *(Ref code98-004-0543)*	1.3% *(Ref code. 98-005-2230)*
Thenardite	Na_2SO_4	Absent	1.4% *(Ref code. 98-002-7654)*

The presence of the mineral thenardite in the NAM, as represented by the XRD pattern in Figure 4-3, is attributed to the formation of sodium sulphate (Na_2SO_4). This compound was formed by the surfactant interacting with the eggshell powders during ball milling. A point deserving of mention is that thenardite occurs naturally as an anhydrous sodium sulphate and is known to provide good stability and high solubility in water. As shown by the XRD pattern (Figure 4-3), it can be inferred that the NAM will be soluble in water. This is critical, as abrasive material is generally used in slurry form when polishing removable dental appliances. Furthermore, XRD analysis of eggshell powder and the NAM revealed distinct calcium carbonate patterns thereby indicating that both materials have high levels of carbonate (Figure 4-3). This is different from mined and precipitated calcium carbonates, which usually have undesirable concentrations of other elements (Brand-Garnys 2014).

4.1.3 Micro-Analysis and Visual Characterisation of Particle size and Shape of NAM

The histograms and S-curves in Figure 4-6 represent three different particle size distributions of the NAM. The average mean size of the NAM in Figure 4-6 A, B and C measured 50nm, 0.3µm and 44µm, respectively. This measurement range in particle size is similar to pumice *(See Table 3-2 in Chapter 3 and Addendum 7)* and is in line with ASTM, FEPA and ANSI/ADA recommended standards for abrasives. From a

[3] The numbers cited are International Centre for Diffraction Data (ICDD) reference codes, which serves as the reference standard for XRD analysis. This code helps to identify organic and inorganic crystalline material.

dental material science perspectives, it can be gathered that the 50nm and 0.3µm particle sizes can be characterised as a superfine dental abrasive material. The 44µm particle size can be typified as medium dental abrasive material. This is consistent with Anusavice and Antonson (2013).

The SEM images (Figures 4-5 and 4-6) showed that the NAM particles are irregular in shape with a sponge-like structure. This is further supported by the TEM micrograph (Figure 4-7), which shows angular-shaped NAM particles. This irregular particle shape is considered to be effective in achieving higher polished surfaces (O'Brien 2002). A noteworthy result as depicted by the TEM image in Figure 4-8 is that the nanoparticles are clustered together, thereby causing particle agglomeration in the NAM. This correlates with the earlier work of Stehr (1988), in that particle agglomeration is a common phenomenon in ball milled nanomaterials.

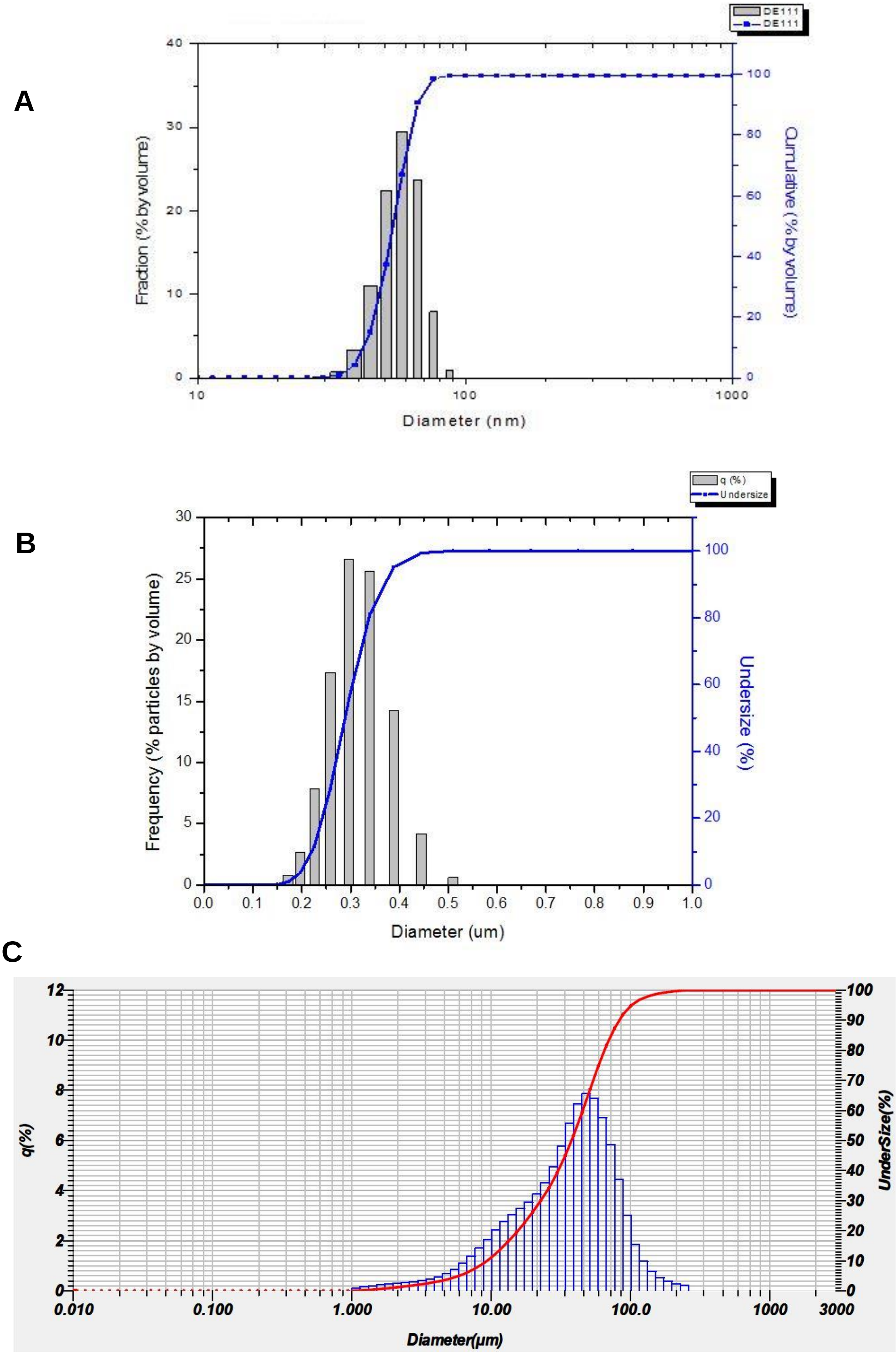


Figure 4-4: Particle size distribution of NAM - **(A)** nano; **(B)** fine; **(C)** medium size.

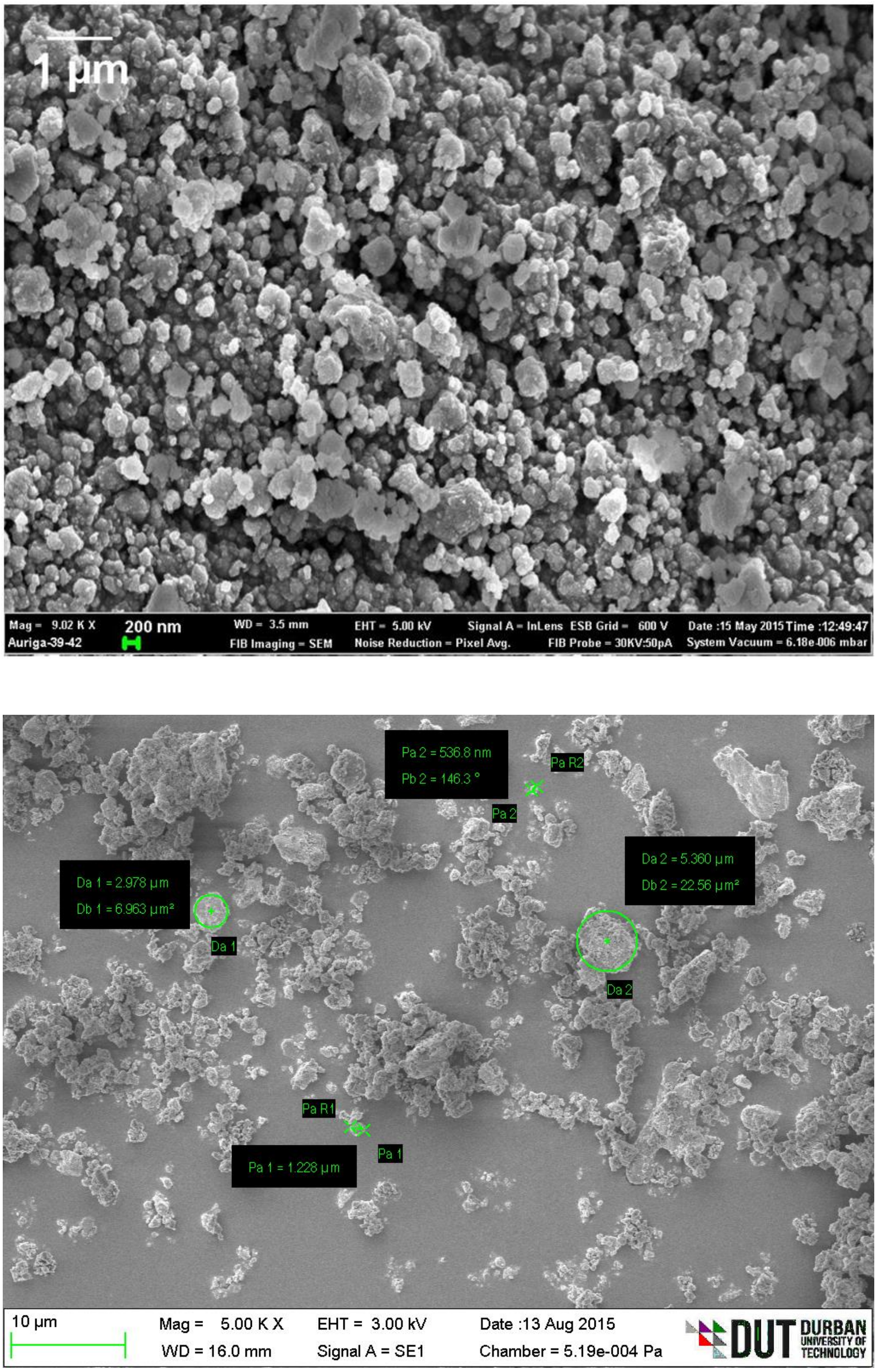
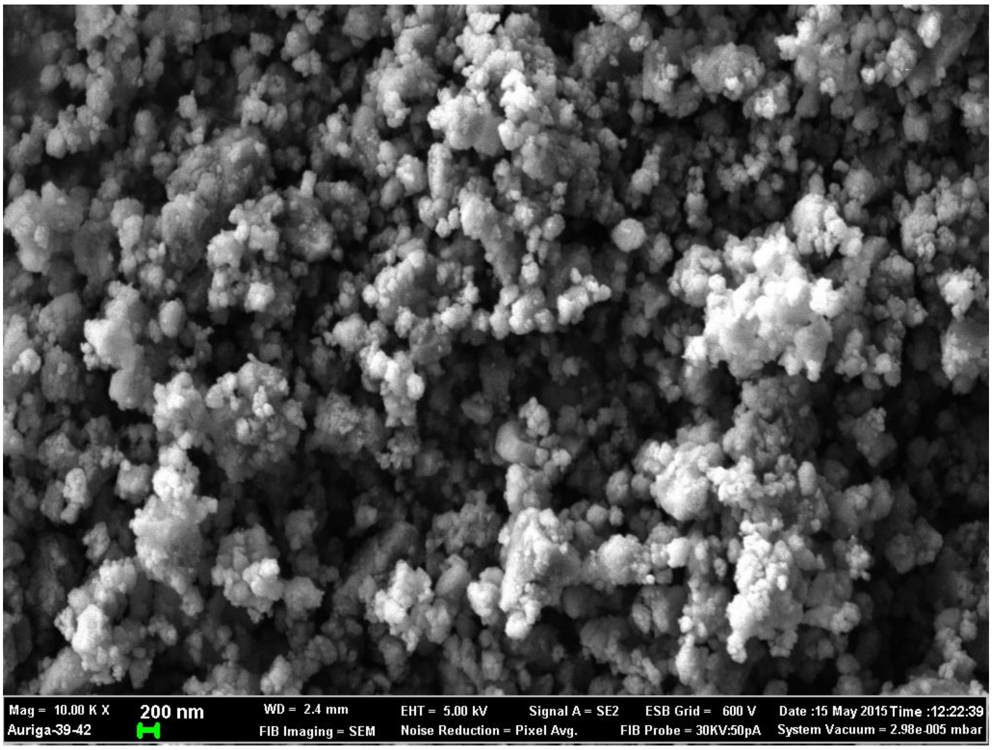


Figure 4-5: SEM images of NAM showing particle shapes and micron sizes at different magnifications.



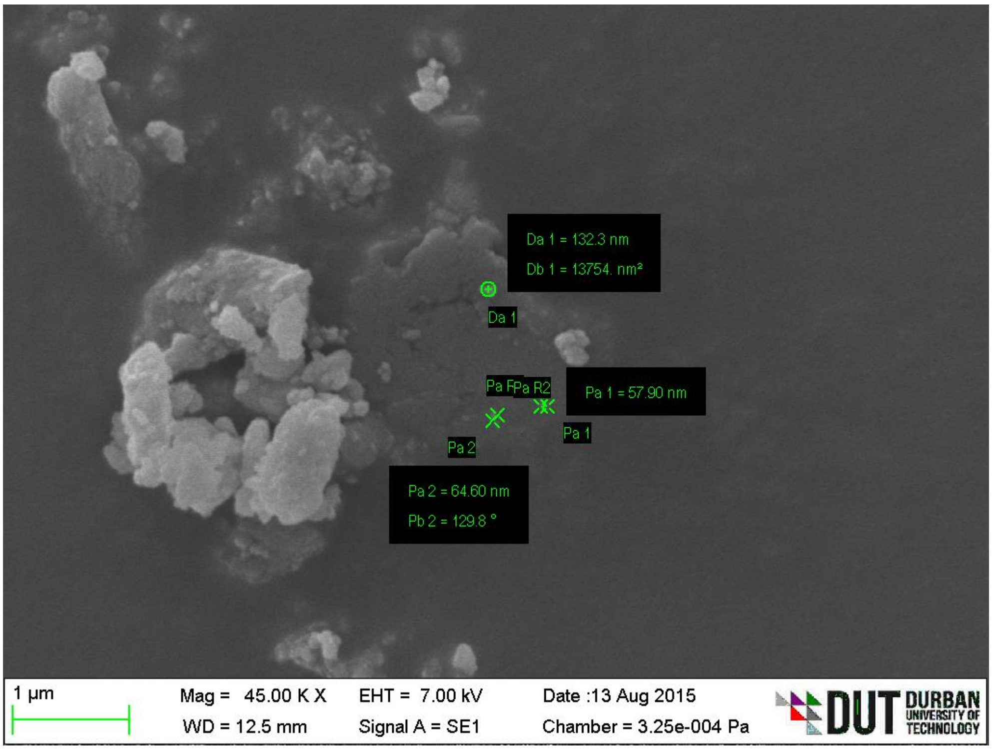


Figure 4-6: SEM images of NAM showing particle shapes and nano sizes at different magnifications.

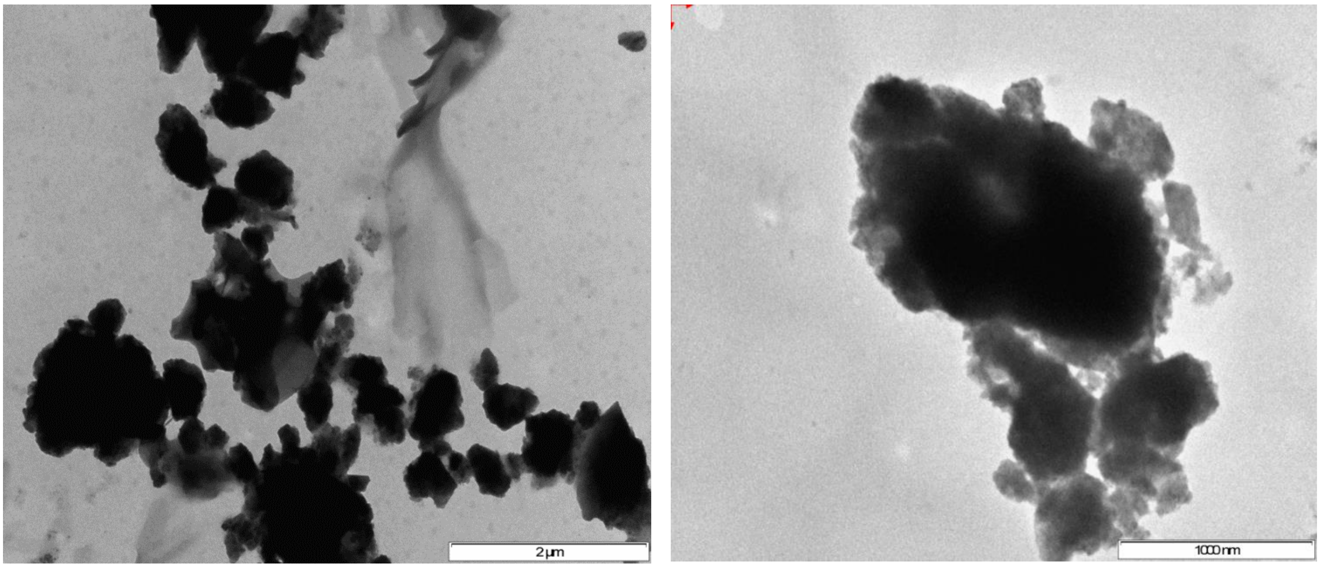


Figure 4-7: TEM micrograph of NAM in microns.

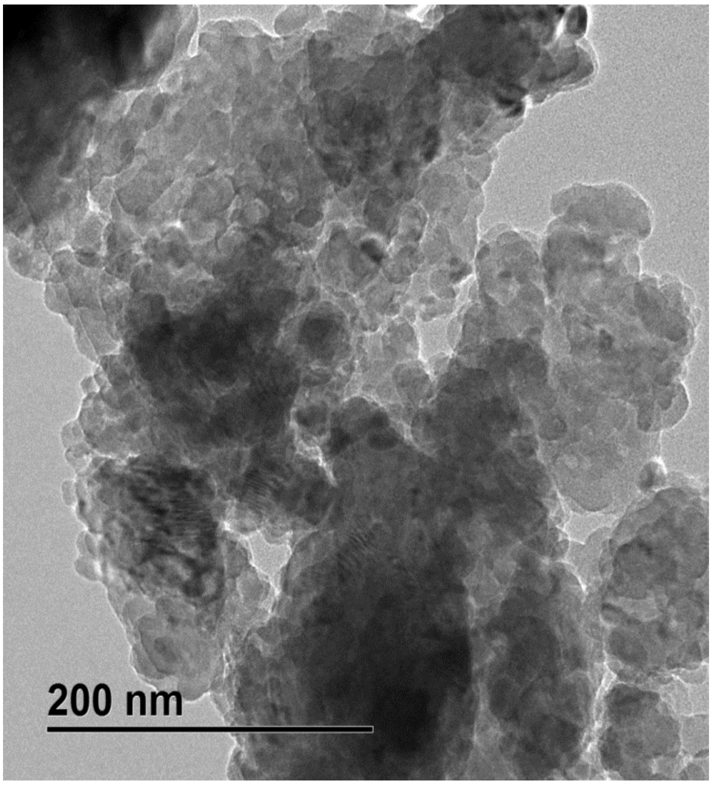


Figure 4-8: TEM Micrograph of NAM showing particle agglomeration.

4.1.4 Thermal Stability and Degradation of NAM

From Figure 4-9 the TGA curves show the incidence of three thermal events within the temperature range of 50-900^{o}C. The first phase (65^{o}C) is endothermic. This is attributed to the removal of absorbed moisture from the NAM particles, which caused a small weight loss (~ 1.0%). The second phase (550^{o}C) is exothermic. Here, there is a 3.7% weight loss caused by the decomposition of organic substances. The third phase (699.14^{o}C) is endothermic, and is linked to the decomposition of calcium carbonate to carbon dioxide and calcium oxide. This weight loss equated to approximately 42.4% of the total mass.

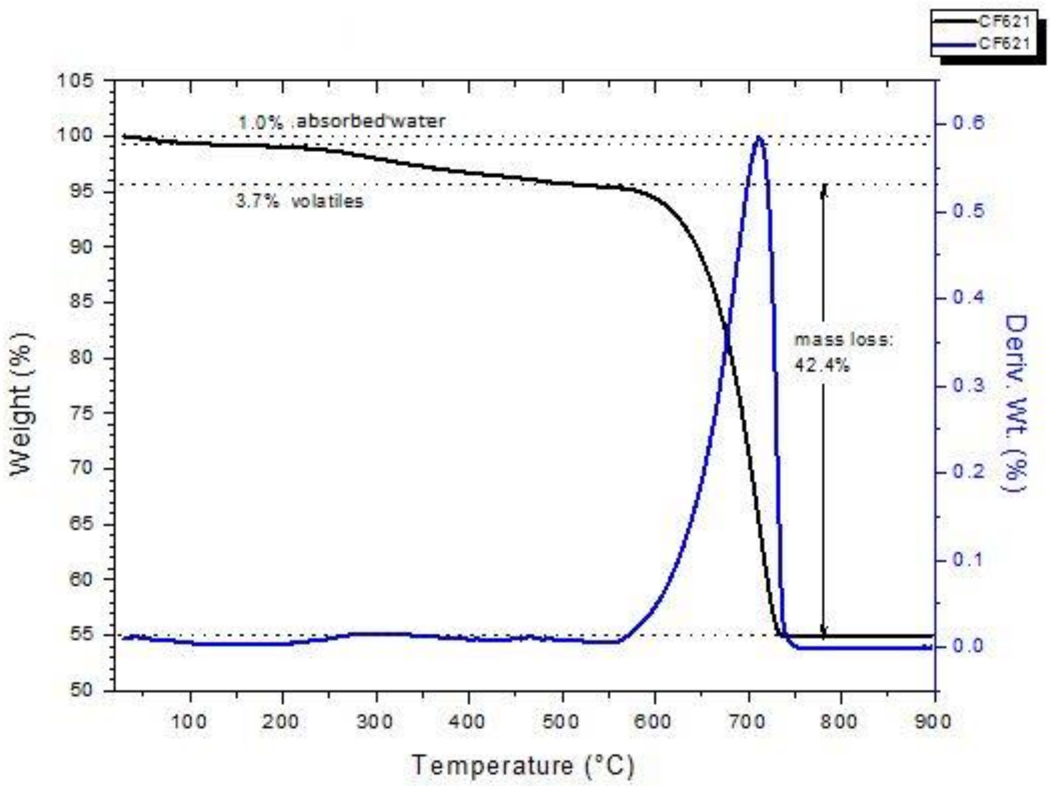


Figure 4-9: TGA curves of NAM.

In addition, and as advocated by (de Beer *et al.* 2015), the equation below was used to calculate the purity of $CaCO_3$ constituent of the NAM. Note that MW denotes molecular weights of $CaCO_3$ and CO_2 and Wt% represents the weight loss of the sample.

$$P_{caco_3}\ (\%) = Co_2\ (wt\ \%) \times MW_{caco_3}/MW_{co_2}$$

The purity of the $CaCO_3$ in the NAM is 96.3%, which is higher than the benchmark of 90.0% for high grade $CaCO_3$ (Oates 1998). This suggests that in terms of purity the

NAM can be used as dental abrasive material, which is demonstrated in phase two of this study.

4.2 Metal Ions in NAM

Table 4-3 and Figure 4-10 illustrate the elemental composition of the NAM. High levels of carbon, oxygen and calcium are evident, which is attributed to the main component of eggshells, being calcium carbonate. This result correlates with the XRD analysis in Figure 4-3.

Table 4-3: EDX elemental composition of NAM.

Element	Weight in percentage (%)
C	21.44
O	53.33
Na	0.28
Mg	0.46
Al	0.08
P	0.47
Ca	23.93
Total	100.00

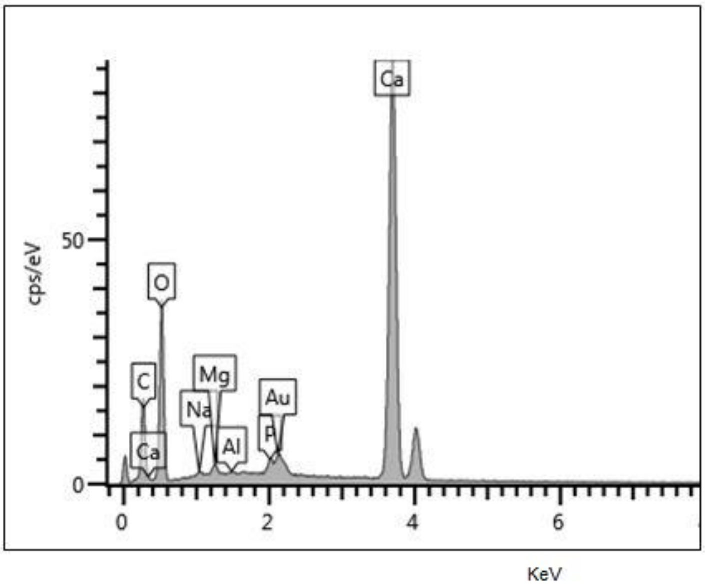


Figure 4-10: EDX spectrum of NAM.

Furthermore, and apart from the high Ca content (48%), ICP-OES measurements revealed low traces of Al, Mg and Si in the NAM (Table 4-4). The high content of Ca detected could be linked to the decomposition of calcium carbonates around 700ºC and the subsequent loss of carbon dioxide to the atmosphere.

Table 4-4: ICP-OES analysis of NAM.

Element	% Weight
Al	0.05
Ca	48
Mg	0.87
Si	0.01

The HPLC identification and quantification shown in Figures 4.11 and 4.12 revealed the presence of Linear Alkylbenzene Sulfonate (LAS). This was deducted by the retention time of 1.83 and the peak area from chromatogram (424206.47), which is indicative by the retention time of Linear Alkylbenzene Sulfonate (LAS). This aligns to ISO standard 13.0 (2001). A point worth mentioning is that the calculated concentration of LAS in NAM was 11.19ppm. Consistent with Davies (1992), this result indicates that the NAM is within environmental safety limits.

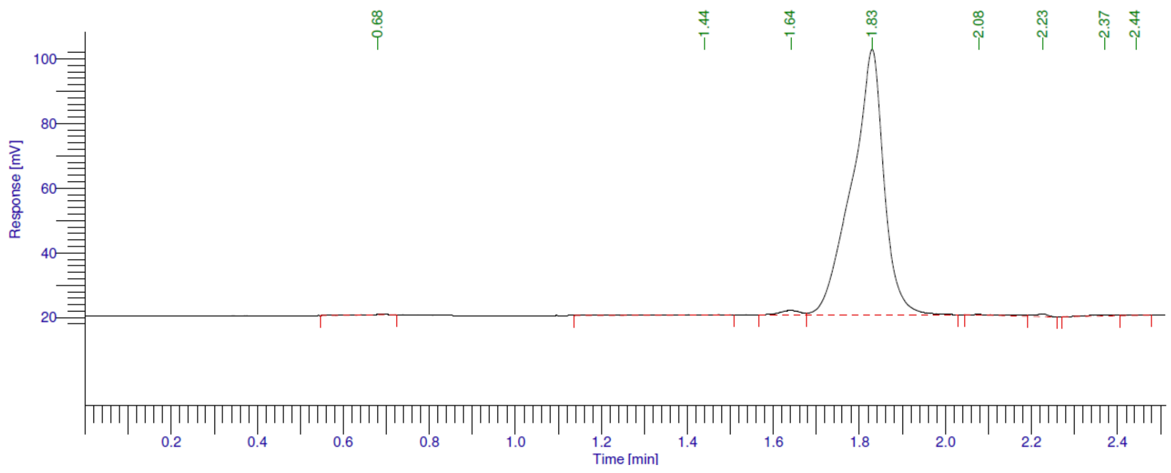


Figure: 4-11: HPLC Identification of Linear Alkylbenzene Sulfonate.

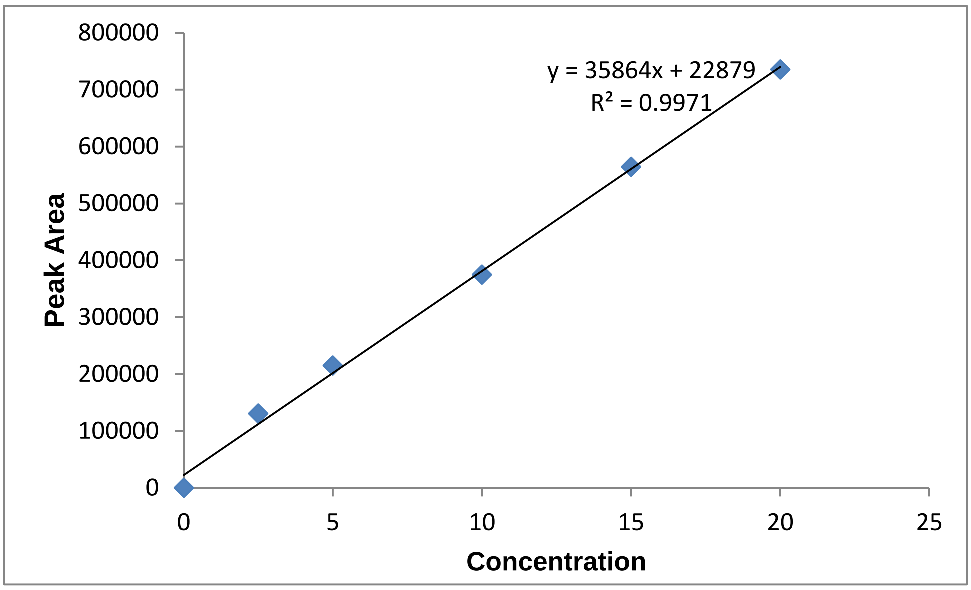


Figure 4-12: Quantification of Linear Alkylbenzene Sulfonate in NAM.

Overall, and as deducted from the foregoing section, the most salient feature is that the NAM is a pure calcite material which is free of heavy or toxic metals. As per the product safety guidelines of the Chinese Medicine Board (2004), European Commission (2009) and ISO/TR 17276 (2014), the NAM is deemed to be safe to use as an abrasive material.

4.3 Microbial Contamination in NAM

Before discussing the results on the levels of microbial contamination in the NAM, the reason for typifying the NAM as a cosmetic product is first needed. As stated by the DEPA (Detmar *et al.* 2010), a cosmetic is any substance or preparation intended to be placed in contact with the various parts of the human body, including the teeth and the mucous membranes of the oral cavity. In light of this explanation, and given that removable appliances are manually manipulated by dental technicians, evaluating the microbial limit of the NAM against the recommended guidelines for cosmetic products is necessary. Although cosmetic products are not expected to be aseptic, Hitchins, Tran and McCarron (2001) reported that they must be completely free of high-virulence microbial pathogens. The total number of aerobic micro-organisms per gram must also be low. Table 4-4 presents the microbial limits for pathogens in cosmetic products, which is used as a guideline in this study.

Table 4-5: Microbial limits for pathogens in cosmetic products.

Pathogens	[1]FDA	[2]DEP	[3]Chinese Medical Board
	Colony forming units/gram (cfu/g/ml)		
Total aerobic microbial count	5^2-10^2	10^2	30000
Total yeast and mould count	5^2-10^2	10^2	100

Sources:
[1]Food Drug Administration (FDA) (2001).
[2]Danish Environmental Protection Agency (Detmer *et al.* 2010).
[3]Chinese Medical Board (Chinese Medicine Board 2004).

In comparison to Table 4-5, the total heterotrophic bacterial and fungal numbers shown in Tables 4-6 and 4-7 were extremely low or non-existent in the NAM. The reasons for the low or non-existent microbial activity in the NAM could be attributed to disinfecting and vacuum drying the eggshells prior to ball milling. This is in agreement with previous findings by Sawai (2003) and Suzuki *et al.* (2006). Another reason for the very low microbial count is that the predominant inorganic mineral (calcium carbonate) is by its very nature a poor source of nutrients for microbes to colonise. This supports the work of Sepehrnia *et al.* (2012), that calcium carbonate inhibits the colonisation of bacteria.

Table 4-6: Total heterotrophic bacteria count in the NAM.

Temperature	100 (g/ml)	10 (g/ml)	1 (g/ml)	0.1 (g/ml)	0.01 (g/ml)
30°C	0.006	0.001	0	0	0
37°C	0	0	0	0	0

Table 4-7: Total fungi count in the NAM.

Temperature	100 (g/ml)	10 (g/m)l	1g/ml	0.1g/ ml	0.01g /ml
30°C	0.013	0.014	0	0	0
37°C	0.17	0.015	0.001	0	0

4.4 Cost Comparison between NAM and Pumice

As outlined in Chapter 1, Section 1.3, an objective of the study was to illustrate the overall cost of pumice and the NAM. Using the mathematical calculation highlighted in Chapter 2, Section 2.8, Table 4-8 presents the cost of production between the two abrasive materials. Evidently, the costs associated in developing the NAM were much lower than pumice, thereby proving to be a more viable alternative.

Table 4-8: Production costs of the NAM and Pumice.

Parameters	NAM	Pumice
Test Area (m^2)	50mm x 20mm x 3mm	50mm x 20mm x 3mm
Time (Min)	2	2
Consumption (Kg/hr)	1.8	1.8
Efficiency (Kg/m^2)	1.7%	1.7%
Abrasive rate (m^2/hr)	Constant	Constant
Cost (Rand/per Kg)	R28.45	R157.68
Disposal (tonne)	Constant	Constant
Total cost (R/m^2)	R1779.4	R16695.5

Note: The abrasive rate and disposal cost of NAM and pumice were both constant. Hence, these costs would not have impacted on the Total cost calculated for NAM and pumice.

Overall, Phase One was premised on characterising an alternative abrasive material synthesised from eggshells in order to ascertain its use as an abrasive material. Both FTIR and XRD analyses confirmed that the NAM was pure calcite with unique water absorbing characteristics, and is free of bacteria. The enhanced physical and chemical characteristics of the NAM confirms the product's application as an alternative abrasive material to pumice to polish removable dental appliances. The TGA analysis further indicated that the high grade carbonate in the NAM is thermodynamically stable, which makes it suitable for use as an abrasive product. The next phase tests the research hypothesis by demonstrating the qualities of the NAM in reducing the surface roughness of PMMA resins.

4.5 Phase Two – Main study

4.5.1: Surface roughness analysis

Figure 4-13 illustrates the surface roughness value of the PMMA specimens at each abrasive application stage, that is: grinding the specimens with a tungsten carbide bur; smoothening the specimens with silicon carbide; polishing the specimens using the NAM; and polishing the specimens using pumice. The surface roughness of the PMMA specimens at each abrasive application stage was significantly different (p<0.001).

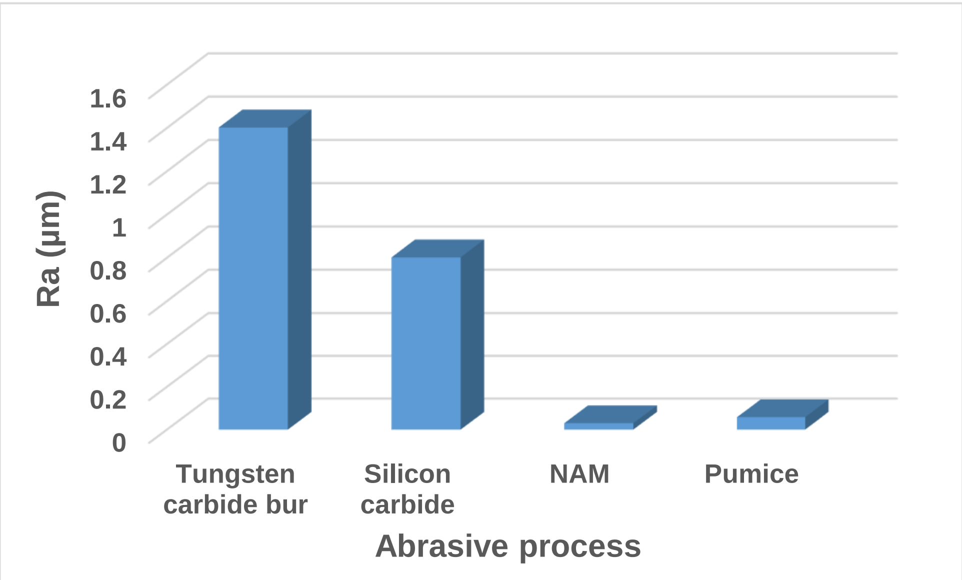


Figure 4-13: Mean difference of surface roughness reduction at each processing stage.

The normal distribution of the R_a values are presented in Table 4-9. The Kolmogorov-Smirnov (KS) test for normality revealed significant differences against the normality of the R_a values ($p<0.05$). This means that the surface roughness (R_a) value of the PMMA specimens polished with the NAM and pumice were skewed (Table 4-10). It can be inferred that the mechanised polishing used in the main phase ensures uniformity and consistency in the polishing of the PMMA specimens.

Table 4-9: Normal distribution of the R_a values.

Polishing Material	*Degree of freedom (df)*	Kolmogorov-Smirnov (KS)
		p-value
NAM	50	0.000
Pumice *(control)*	50	0.011

The Levene's test for equality of variance, t-test, mean, standard deviation, and standard error results are shown in Table 4-11. As indicated by the levels of significance, both Levene's test and t-test revealed that the surface roughness (R_a) values for the PMMA specimens exhibited statistically significant differences between the NAM and pumice ($p<0.0001$). As illustrated in Figure 4-14, the control group had the highest R_a mean values (0.1056±0.03688µm), while the PMMA specimens polished with the NAM had the lowest R_a mean values (0.0476±0.01379).

Table 4-10: Surface roughness (R_a) values of PMMA specimens polished with NAM and pumice.

PMMA Specimen Number	Ra value of PMMA specimens polished with NAM	Ra value of PMMA specimens polished with pumice
1	0.06µm	0.08µm
2	0.04µm	0.10µm
3	0.04µm	0.11µm
4	0.05µm	0.09µm
5	0.06µm	0.09µm
6	0.07µm	0.16µm
7	0.08µm	0.13µm
8	0.07µm	0.13µm
9	0.07µm	0.15µm
10	0.07µm	0.15µm
11	0.03µm	0.06µm
12	0.05µm	0.06µm
13	0.04µm	0.06µm
14	0.03µm	0.05µm
15	0.04µm	0.06µm
16	0.07µm	0.15µm
17	0.03µm	0.12µm
18	0.04µm	0.11µm
19	0.03µm	0.10µm
20	0.04µm	0.12µm
21	0.05µm	0.10µm
22	0.06µm	0.09µm
23	0.05µm	0.15µm
24	0.04µm	0.08µm
25	0.04µm	0.08µm
26	0.03µm	0.12µm
27	0.02µm	0.08µm
28	0.03µm	0.08µm
29	0.03µm	0.08µm
30	0.03µm	0.10µm
31	0.05µm	0.14µm
32	0.05µm	0.12µm
33	0.07µm	0.12µm
34	0.05µm	0.12µm
35	0.05µm	0.12µm
36	0.03µm	0.11µm
37	0.05µm	0.11µm
38	0.05µm	0.13µm
39	0.03µm	0.11µm
40	0.05µm	0.11µm
41	0.05µm	0.11µm
42	0.05µm	0.11µm
43	0.05µm	0.13µm
44	0.05µm	0.11µm
45	0.05µm	0.10µm
46	0.05µm	0.05µm
47	0.05µm	0.04µm
48	0.06µm	0.04µm
49	0.04µm	0.03µm
50	0.06µm	0.03µm

Table 4-11: Independent sample test.

Polishing Material	Mean	Std. deviation	Std. Error	Levene's test *(p<0.05)*	t-test *(p<0.05)*
NAM	0.0476	0.01379	0.00195	0.000	0.000
Pumice *(control)*	0.1056	0.03688	0.00522		

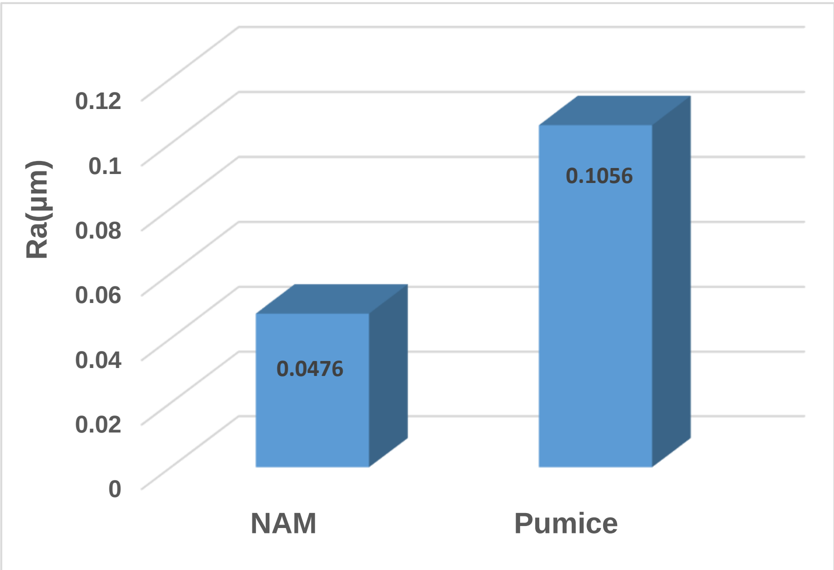


Figure 4-14: Difference in mean surface roughness values between polishing materials.

4.5.2 Microscopy observations

As illustrated in Figures 4-15 and 4-16, Optical Electron Microscope (OEM) and Scanning Electron Microscope (SEM) images of the PMMA specimens visibly confirmed the differences between the polished and unpolished surfaces.

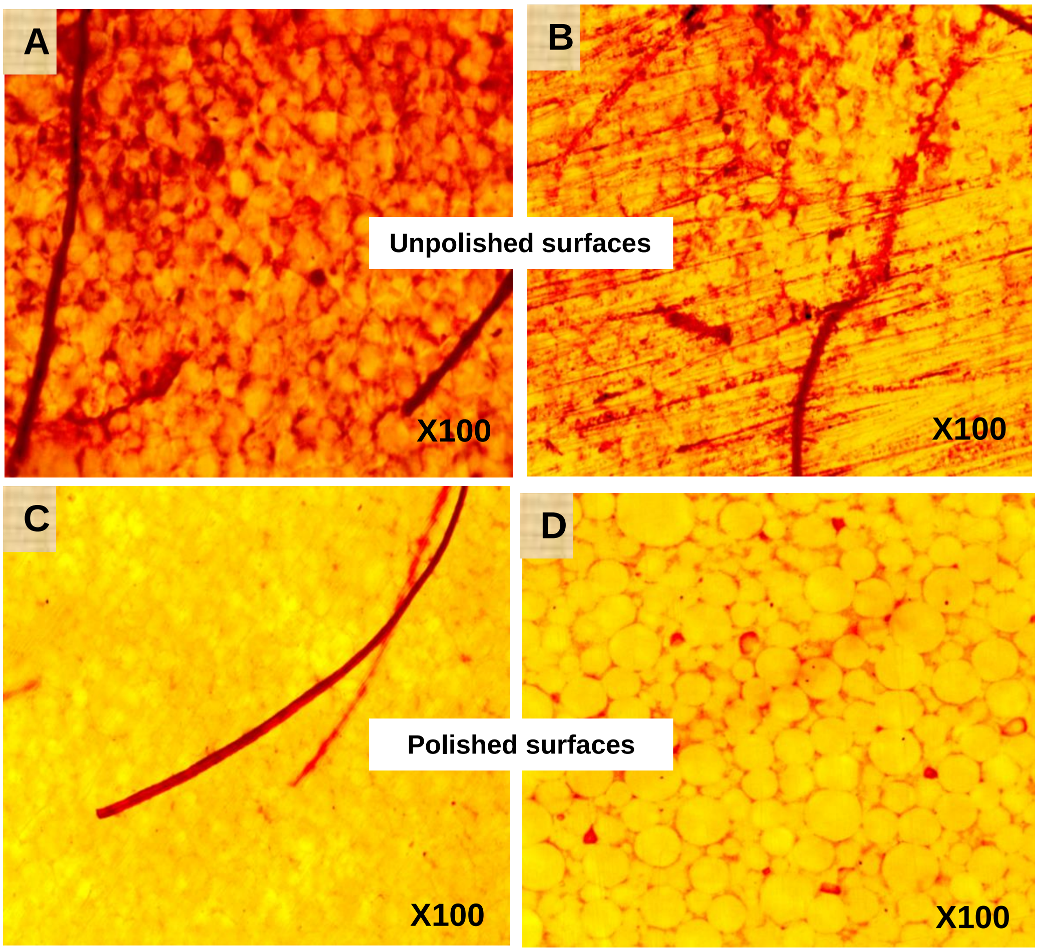


Figure 4-15: OEM images (x100 magnification) of the polished and unpolished PMMA resins surfaces: **(A)** rimmed with tungsten carbide bur; **(B)** sand-papered with silicon carbide after trimming; **(C)** sand paper followed by pumice 5-8µm; **(D)** sand paper followed by NAM ≤0.3µm

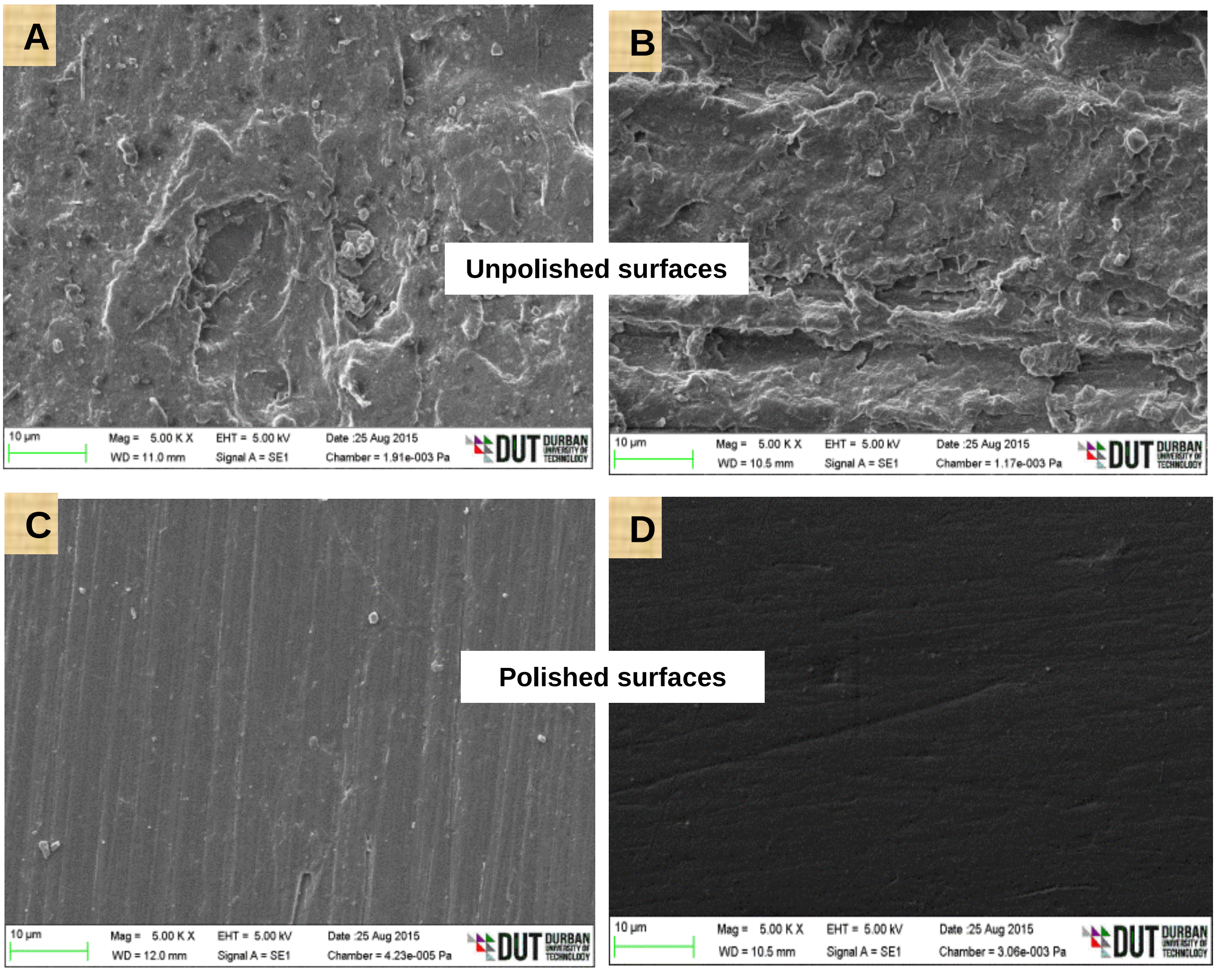


Figure 4-16: SEM images (x5000 magnification) of the polished and unpolished PMMA resins surfaces: **(A)** rimmed with tungsten carbide bur; **(B)** sand-papered with silicon carbide after trimming; **(C)** sand paper followed by pumice 5-8µm; **(D)** sand paper followed by NAM ≤0.3µm.

4.5.3 Discussion of the Results

In light of the aforementioned results, the hypothesis as outlined in Chapter One, Section 1.4, was accepted as the NAM significantly reduced the surface roughness (R_a) of the polished specimens (p<0.001). Importantly, the R_a values of all the PMMA specimens were below the acceptable threshold limit value of 0.2µm, thereby confirming that the NAM effectively reduces surface roughness. Contrary to harder abrasive materials such as pumice (Mohs hardness 6-7) providing smoother polished surfaces (Bassam, Alaa and Wael 2008; Anusavice and Antonson 2013), the results of this study revealed that the NAM (R_a=0.0476µm) is more likely to produce better polished surfaces than pumice (R_a= 0.1056µm). Arguably, the improved polished surfaces of the PMMA specimens could be attributed by the surfactant composition of the NAM. As indicated in Phase One the presence of the mineral thenardite holds the NAM particles tightly together, thereby quickening the abrasion process.

Moreover, the different particle sizes of the NAM and pumice (Table 3-2) contributed to the significant differences in the R_a values. This supports the argument of Bassam, Alaa and Wael (2008) that abrasive materials of smaller particle sizes, as present in the NAM, quickly exposes newly-formed and sharper particles during the abrasion process and subsequently reduces surface roughness rapidly. This conforms to the principles of abrasion that is harder materials such as the NAM come into frictional contact with a substrate, which in this study were the PMMA specimens. Consequently, tensile and shear stresses are generated which facilitate a reduction of surface roughness. Additionally, the R_a value of pumice (0.10µm) reported in this study correlates with Al-Kheraif (2014), which confirms that the mechanised polishing method was reliable.

The OEM and SEM images in Figures 4-15 and 4-16 show visible differences in the polished PMMA specimen surfaces at different magnifications. The low magnification of the polished PMMA specimen surface in Figure 4-15 showed no visible scratches. In contrast, and at a higher magnification (Figure 4-16), scratches were visible on the polished PMMA specimen surfaces. This corroborates with Anusavice and Antonson (2013) that abrasive particles in the range of fine particle sizes provide lustre at a low magnification, whereas at higher magnification scratches are detectable. The results of this study therefore confirm that polishing processes do not necessarily eliminate but can only reduce surface roughness. It is important to note that in clinical practice highly smoothened surfaces are generally good indicators of surface lustre of polished dental prostheses, which are assessed without magnification.

Overall, the salient features of this study demonstrated that the NAM effectively reduced the surface roughness of the PMMA specimens to below the threshold limit value of 0.2µm. The R_a values also favourably linked to below the threshold limit value of 0.2µm, which suggested that the particle size of the NAM used in this study provided clinically acceptable polished surfaces. This correlates with several authors (Quirynen and Bollen 1995; Kuhar and Funduk 2005; Moura *et al.* 2006; Satpalty, Dhakshaini and Gujjari 2013; Al-Kheraif 2014) that the lower the threshold limit value, the lesser will be the accumulation of plaque on removable appliances. Ultimately, and by associating the R_a values to the threshold limit value of 0.2µm, the NAM has proven to be a better product than pumice. The next chapter will provide the conclusions drawn from this study. This will include the identification of limitations, which will steer the study for future research.

Chapter Five – Conclusion and Recommendations

The focus of this study was to use eggshells, a natural waste product, to develop and test the quality of an alternative abrasive material to reduce the surface roughness of heat-cured acrylic resins. A quantitative research approach and an experimental research design was adopted. In phase one of this study different characterisation techniques were used to assess the suitability of the new abrasive material (NAM). Phase two, by contrast, investigated the quality of the NAM as an abrasive material for removable dental appliances. This chapter concludes by drawing on the discussion of the aforementioned phases to provide recommendations by proposing directions for future research.

5.1 Conclusions

The findings of this study have explicitly underlined the different characterisation methods (BET; FTIR; XRD; EDX; SEM; TEM; and PSA) to show that eggshell waste can be used to develop a value added product which can naturally replace calcite, a mineral generally mined and used as a dental abrasive material. This is in line with achieving objective 1.3.1.1 that is to determine the physical characteristics of the NAM in terms of crystallisation; hardness; pore volume; particle size and surface area; to establish the abrasive and strength qualities of the materials.

TGA analysis further confirmed that the high grade carbonate in the NAM makes it a suitable and economically viable alternative for abrasive applications. This is in line with achieving objectives 1.3.1.2, that is to determine the levels of degradability and stability of the material by conducting thermal analyses of the NAM.

In particular, and in terms of achieving objective 1.3.1.5, which was to determine the production costs of developing the NAM in comparison with pumice. The associated low cost of developing the NAM will significantly reduce the problems of cross-contamination in re-using other abrasive materials such as pumice in dental laboratories, both in developing and developed countries.

In terms of the safety of the product, and in line with achieving objective 1.3.1.4, that is to determine the chemical constituents of the NAM in order to identify the different metal ions. The prominent aspects of this study confirm that the NAM is free of heavy or toxic metals.

In addition, and in terms of objective 1.3.1.3, which was establish the level of bacterial contamination in order to ascertain the microbial contents of the NAM. The microbial analysis of the NAM revealed that it is free from virulent pathogens and bacterial contamination.

Notably, and in line with achieving objective 1.3.2.1 and 1.3.2.2 in phase two, this study conclusively showed that the NAM effectively reduces the surface roughness to below the threshold limit value of 0.2µm. This further confirmed that the particle size of the NAM used in this study provided clinically acceptable polished surfaces.

A point deserving mention is that in spite of the mechanised polishing methods providing valuable and consistent results in this study, this method has its limitation. In particular, and from a dental technology laboratory perspective, appliances are made to fit different patient's mouths. Hence, mechanised polishing cannot be applied.

5.2 Recommendations

A constraint that emerged through the results of this study was particle agglomeration, which is inextricably linked to the ball milling process. This is an area for further research. Equally significant, abrasive materials are used both intraorally as dental prophylaxes for polishing tooth enamel, and extraorally to polish dentures. This study only focused on the extraoral use. Future research could therefore explore using eggshell and titanium oxide nanoparticles to develop dental prophylaxes. Nanotechnology research in this area of work is an unchartered territory and will therefore encourage the development of novel solutions in the field of healthcare, cosmetics, and abrasive applications. Additionally, altering the molecular and atomic structure could potentially improve nanomaterial properties, which may not be possible in their original state. This supports future investigations into finding improved methods of synthesising nanoparticles while minimising the rate of agglomeration.

Additionally, future research work will involve pre- and post-tests of mechanised polishing to further determine the efficacy of NAM. SEM and TEM analyses will be used to achieve this.

Finally, the results of this study have enabled the researcher to forward a patent application for the NAM. Potentially this could attract external funders to support the development of other, and more advanced, dental materials using natural waste.

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Addendum 1: Ethical Clearance Letter

DUT DURBAN UNIVERSITY OF TECHNOLOGY

Institutional Research Ethics Committee
Faculty of Health Sciences
Room MS 49, Mansfield School Site
Gate 8, Ritson Campus
Durban University of Technology

P O Box 1334, Durban, South Africa, 4001

Tel: 031 373 2900
Fax: 031 373 2407
Email: lavishad@dut.ac.za
http://www.dut.ac.za/research/institutional_research_ethics

www.dut.ac.za

10 September 2015

IREC Reference Number: **REC 60/15**

Mr S C Onwubu
12 Taiwo Odekunle
Close by Coker Road
Off Orimolade Bus Stop
Ifako-Ogba
Lagos State
Nigeria

Dear Mr Onwubu

Using eggshell for the development of a quality alternative material to pumice in reducing the surface roughness of heat-cured acrylic resins

The Institutional Research Ethics Committee acknowledges receipt of your gatekeeper permission letters.

Please note that FULL APPROVAL is granted to your research proposal. You may proceed with data collection.

Yours Sincerely,

[redacted]

Professor M N Sibiya
Deputy Chairperson: IREC

DUT DURBAN UNIVERSITY OF TECHNOLOGY
2015 -09- 10
INSITUTUTIONAL RESEARCH ETHICS COMMITTEE
P O BOX 1334 DURBAN 4000 SOUTH AFRICA

Addendum 2: IREC Permission Letter

Directorate for Research and Postgraduate Support
Durban University of Technology
Tromso Annexe, Steve Biko Campus
P.O. Box 1334, Durban 4000
Tel.: 031-3732576/7
Fax: 031-3732946
E-mail: moyos@dut.ac.za

8th September 2015

Mr Stanley Onwubu
c/o Department of Dental Sciences
Durban University of Technology

Dear Mr Onwubu

PERMISSION TO CONDUCT RESEARCH AT THE DUT

Your email correspondence in respect of the above refers. I am pleased to inform you that the Institutional Research Committee (IRC) has granted permission for you to conduct your research "Using eggshell for the development of a quality alternative material to pumice in reducing the surface roughness of heat cured acrylic resin" at the Durban University of Technology.

Kindly note, that the committee requires you to provide proof of full ethical clearance prior to you commencing with your research at the DUT.

We would be grateful if a summary of your key research findings can be submitted to the IRC on completion of your studies.

Kindest regards.
Yours sincerely

[redacted]

PROF. S. MOYO
DIRECTOR: RESEARCH AND POSTGRADUATE SUPPORT

Addendum 3: Information and Consent Letter

LETTER OF INFORMATION

Title of the Research Study: Using eggshell for the development of a quality alternative material to pumice in reducing the surface roughness of heat-cured acrylic resins

Principal Investigator/s/researcher: Mr Stanley Onwubu (B Tech: Dental Technology)

Co-Investigator/s/supervisor/s: Dr Anisa Vahed (D Tech: Quality, Dr Shalini Singh (D Tech: Quality and Prof Krishnan Kanny Phd (Material Sciences and Engineering).

Brief Introduction and Purpose of the Study:

The university and those conducting this task subscribe to the ethical conduct of academia and research and to the protection at all times of the interests, comfort, and safety of participants. This form and the information that it contains are given to you for your own protection and full understanding of the procedures. Your signature on this form will signify that you have been informed:

- On the task of assessing the level of smoothness of poly methyl methacrylate acrylic (PMMA) specimens, at first glance;
- On having adequate opportunity to consider the information communicated to you; and
- That participation in the task is voluntarily agree.

Any information that is obtained during this task will be used as per the agreement, viz. that it will be documented for scholarly purposes, and for public information, where relevant and applicable, and only with this prior consent.

Outline of the Procedures:

You are required to assess the level of smoothness, at first eye glance, of the polish poly methyl methacrylate acrylic (PMMA) specimens.

Risks or Discomforts to the Participant:

Kindly note that there are no risks involved whatsoever should you choose to participate in this exercise.

Benefits:

There are no benefits attached to the participants for his or her participation in this study. Kindly be advised that developing an alternative abrasive material will be of value to the Dental Technology industry.

Reason/s why the Participant May Be Withdrawn from the Study:

Kindly note that there will be no adverse consequences for should the participant choose to withdraw from the task.

Remuneration:

There is no remuneration attached for participation. Participation is completely voluntary.

Costs of the Study:

Kindly be advised, there is no costs to the participants in whatsoever for their participation.

Confidentiality: Participants will be anonymous, hence their personal details will not be required.

Research-related Injury:

The exercise will not involve physical or chemical contact. Hence, there is no foreseen injury related incident to the participants for their participation.

Persons to Contact in the Event of Any Problems or Queries:

Contact: Dr Anisa Vahed on 031 373 2848 or the Institutional Research Ethics administrator on 031 373 2900. Complaints can be reported to the DVC: TIP, Prof F. Otieno on 031 373 2382 or dvctip@dut.ac.za

CONSENT

Statement of Agreement to Participate in the Research Study:

- I hereby confirm that I have been informed by the researcher, Mr Stanley Onwubu**,** about the nature, conduct, benefits and risks of this study - Research Ethics Clearance Number: ___________,
- I have also received, read and understood the above written information (Participant Letter of Information) regarding the study.
- I am aware that the results of the study, including personal details regarding my sex, age, date of birth, initials and diagnosis will be anonymously processed into a study report.
- In view of the requirements of research, I agree that the data collected during this study can be processed in a computerised system by the researcher.
- I may, at any stage, without prejudice, withdraw my consent and participation in the study.
- I have had sufficient opportunity to ask questions and (of my own free will) declare myself prepared to participate in the study.
- I understand that significant new findings developed during the course of this research which may relate to my participation will be made available to me**.**

_____________ _________ _______

Full Name of Participant Date Time Signature / Right Thumbprint

I, Mr Stanley Onwubu, herewith confirm that the above participant has been fully informed about the nature, conduct and risks of the above study.

___________ _____ _______________

Full Name of Researcher Date Signature

__________________ ___________ ________

Full Name of Witness (If applicable) Date Signature

__________________ ______________ ___________

Full Name of Legal Guardian (If applicable) Date Signature

Addendum 4: Rating Sheet

Faculty of Health Sciences

Department of Dental Sciences: Dental Technology Programme

Date

Dear Participant,

I am conducting research as part of my Master studies on "Using eggshell for the development of a quality alternative material to pumice in reducing the surface roughness of heat-cured acrylic resins".

Poly methyl methacrylate acrylic (PMMA) specimens will be shown to you. Kindly assess the level of smoothness of these specimens, at first glance. Your responses are to be recorded in Table 1. This task will take approximately ±10 minutes to complete. I will be present to clarify any problems you may experience during this session.

Confidentiality of the information will be respected.

Yours sincerely,

____

Mr Stanley Onwubu
Contact Details
Tel.: 071793085.

____

Supervisor / Promoter
Dr Anisa Vahed
Tel.: 031 373 2848

____

Co-Supervisor/Co-Promoter
Dr Shalini Singh
Tel.: 031 373 5337

____

Co-Supervisor/Co-Promoter
Prof Krishnan Kanny
Tel.: 031 373 2230

Rating Sheet for PMMA Specimens

Kindy rate the level of smoothness of the 10 specimens by placing a Tick "√" in the appropriate block in the Table below:

Table 1: Rating the Level of Smoothness of PMMA specimens

PMMA specimens	Level Of Smoothness Of Poly Methyl Methacrylate Acrylic (PMMA) Specimens, At First Glance			
	Smoothness Ratings			
	Very smooth (4)	Smooth (3)	Rough (2)	Very Rough (1)
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

Addendum 5: Cost of Pumice

Subject:	Re: Cost of Pumice Inquiry
From:	profstan4christ@yahoo.com (profstan4christ@yahoo.com)
To:	jrmike@hesspumice.com;
Date:	Wednesday, June 3, 2015 7:39 PM

From: "Mike Hess Jr." <jrmike@hesspumice.com>

Date: Wed, 3 Jun 2015 09:40:40 -0600

To: <profstan4christ@yahoo.com>

Cc: salesmgr@hesspumice.com<salesmgr@hesspumice.com>;rd@hesspumice.com<rd@hesspumice.com>

Subject: Re: Cost of Pumice Inquiry

Dear Stanley,

We have over 180 grades of pumice if I was to make an average cost of pumice I would have to say $11/lb. The market in the abrasive side of pumice is less than 1 million a year.

Regards,

Mike Hess Jr.

100 Hess Dr.
Malad ID 83252
800-767-4701 ext 147

Addendum 6: Pilot study result - Abrasivity of NAM

Figure 1 illustrates the differences in the time needed to polish the PMMA specimens. Statistically, there were no significant differences in the time needed to polish the specimens ($p > 0.05$). A noteworthy result is that the PMMA specimen polished for two minutes measured the lowest R_a mean value. This time was therefore selected for the main study.

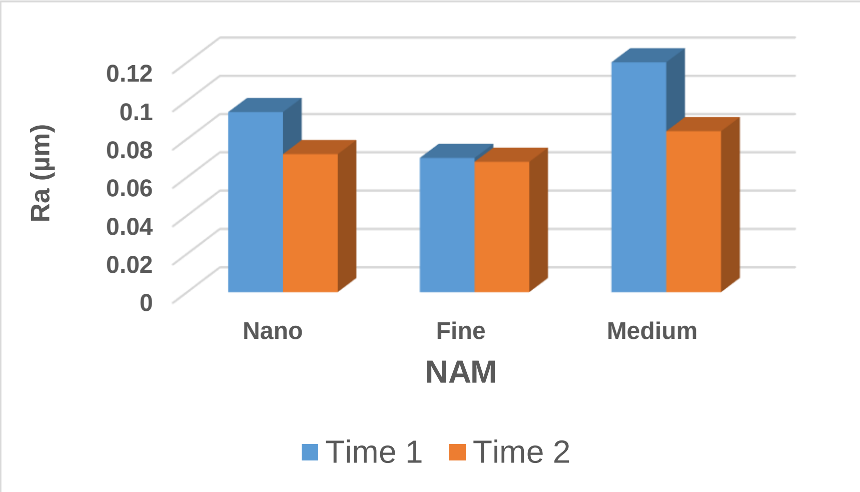

Figure 1: Differences in surface roughness of PMMA specimens using two different polishing times.

As illustrated in Table 2, significant differences ($p<0.001$) were found in the surface roughness for the PMMA specimens polished with the NAM in respect of its particle size distribution. Overall, the medium particle sized NAM (45µm) had the highest R_a mean (0.0783±0.01850µm), while the PMMA specimen polished with the fine particle sized NAM (0.3µm) had the lowest R_a mean values (0.0575±0.01765µm). As shown in Table 3, no significant differences ($p>0.05$) were found between nano, fine and medium particle sized NAM.

Table 2: Statistical results of the different particle sized NAM.

NAM Sample Group	Mean	Std. deviation	Std. Error.	95% Confidence Interval for Mean		ANOVA test (*p* -value)
				Lower Bound	Upper Bound	
Nano	0.0692	0.01676	0.00484	0.0585	0.0798	0.000
Fine	0.0575	0.01765	0.0509	0.0463	0.0687	
Medium	0.0783	0.01850	0.00534	0.0666	0.0901	

Table 3: Tukey and Bonferroni multiple comparison tests.

Multivariate Comparison		Tukey HSD		Bonferroni	
		P-value	Sig.	*P*-value	Sig.
Nano	Fine	0.799	*NS	1.000	NS
Nano	Medium	0.905	NS	1.000	NS
Fine	Medium	0.285	NS	0.518	NS

*NS = No Significant differences.

In addition, and as illustrated in Figure 2, significant differences in the polishing of the specimens were found between the two operators ($p<0.001$). With operator 1, fine particle sized NAM showed the lowest R_a mean value (0.0575±0.01765µm). With operator 2, the medium particle sized NAM had the lowest R_a mean value (0.883±0.02480µm).

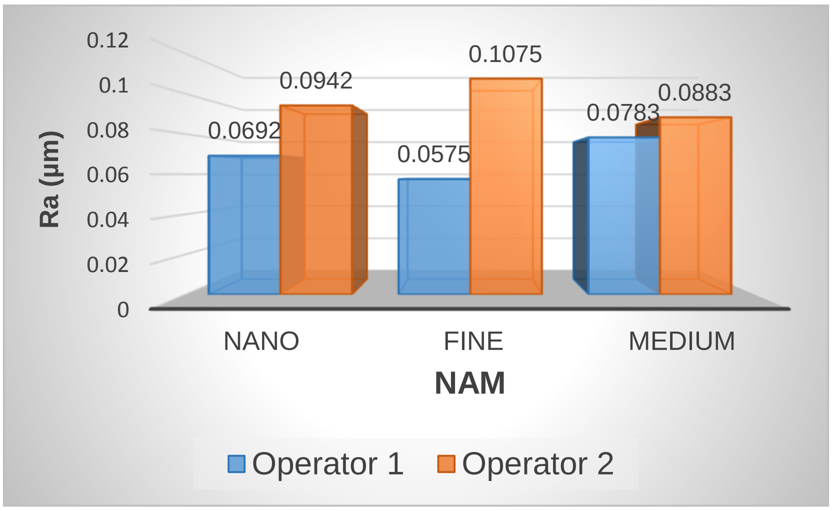

Figure 2: Differences between two operators using the conventional method of polishing.

With reference to the subjective assessment, the majority of the participants (50%) found that the PMMA specimens polished with fine particle sized NAM produced very smooth surfaces (Figure 3). Hence, the fine particle sized NAM was selected for the main study. Another noteworthy finding is that none of the participants rated the polished specimens as being rough.

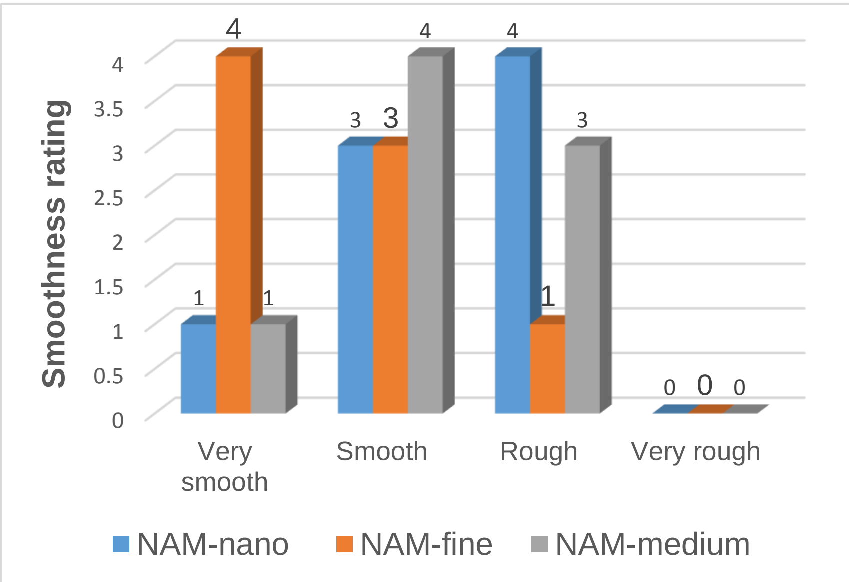

Figure 3: Assessment of Polished PMMA Specimens.

Addendum 7: SEM images of pumice (control)

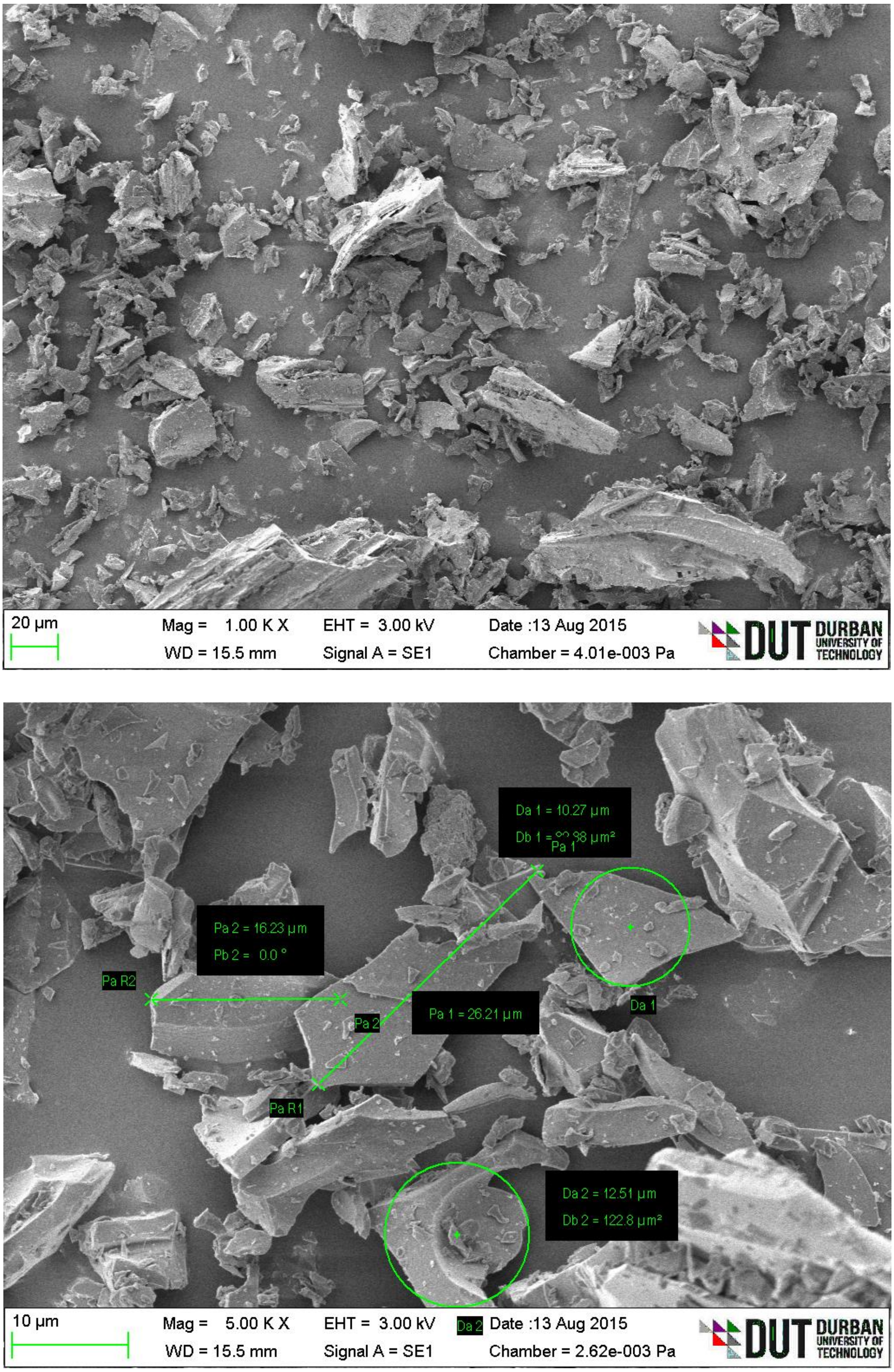

Figure 4: SEM images of pumice showing particle shapes and micron sizes at different magnifications

Addendum 8: Validity and Reliability of Instrument

ZEISS

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

SERVICE REPORT

No.	29972
Order No.	
System No.:	

1 Gillitts Office Park
2 Rodger Place
Gillitts 3610
P.O. Box 954
Kloof 3640
Kwa-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: DUT

Contact: AVINASH
Cell:
Email:
Phone:
Fax:

Description of Fault or Service	Equipment	Model & Serial No	Other serial no.
	EVOHD15-01-19	01-19	
- SERVICE	Software Version	Operating system software	Other
- INSTALL & CALIBRATION OF NEW LAB6 FILAMENT			

Action taken/Service performed..

- INSTALLED NEW FILAMENT
- CALIBRATED AT ALL KV'S
- TESTED AND OKAY
- INSTALLED 300 μM APERTURE
- GUN VACUUM HAS IMPROVED $8E^{-8}$
- SERVICE WENT WELL

DATE	20/10	21/10						TOTALS
LABOUR &	4 hrs	6 hrs						
TRAVEL	1 hrs	1 hrs						
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		
- 300μM 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

Techni[redacted] Customer [redacted] Date 21/10/2015

Carl Zeiss - 25

Minuteman Press Strijdom Park 011 792-8070