A characterisation of the thermal curing and mechanical properties of polymethylmethacrylate / hydroxyapatite composites

by

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Submitted in fulfilment of the requirements of the degree of Master of Technology: Dental Technology in the Faculty of Health Sciences at the Durban University of Technology.

I, Ming Yang, do hereby declare that this dissertation is representative of my own work, both in conception and execution.

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ABSTRACT

Aim

The aim of this study was to investigate the changes in exothermic polymerisation characteristics and a range of mechanical properties in PMMA/HA composites (of varying HA concentrations) against a control sample of pure PMMA.

Methods

Specimens of pure PMMA, and 5, 10, 15, 20 and 25 percent HA composites were made according to the specification of appropriate testing standards using the flask and packing method. Exothermic polymerisation testing was conducted on respective samples using an internal j-type thermocouple temperature sensor. The rate of temperature change and maximum temperature in relation to time were recorded. Mechanical tests included tests of flexural strength and modulus, compressive strength and modulus, tensile strength and modulus and shear strength. All specimens were kept in a controlled environment prior to testing, which was performed on a LIoyd® LR30K universal testing machine, and recorded in computer-generated logs.

Results

Exothermic polymerisation testing revealed a decrease in mean maximum temperature values with increasing HA content. The mean exothermic temperatures of all six groups were above 100˚C, with small relative temperature reductions as the HA percentage increased. The results of mechanical testing revealed that there was a significant reduction in flexural strength in the range between pure PMMA and 15 percent HA and no statistical difference in flexural modulus. There was a notable trend toward a decrease in compressive strength as HA percentage increased, achieving statistical significance at 20 and 25 percent HA, with no statistical difference in compressive modulus between samples. The tensile strength test results no

significant difference between pure PMMA and composites containing up to 15 percent HA. A significant difference was noted between the 20 percent- and 25 percent HA composites and those of lower HA concentration with an increased failure risk as HA concentration was increased above 10 percent. There was a tensile modulus peak at 15 percent HA, and a significant difference between 15 percent HA composites and pure PMMA and the 10 percent HA composite. Shear strength was noted to decrease with HA percentage, with significant reduced strength between the 15 percent HA composite and pure PMMA, as well as between the 20 and 25 percent HA composites and composites of less than 10 percent HA.

Conclusions

The study revealed that the addition of HA to pure PMMA negatively affects the mechanical strength measured in compression, bending or shear. Tensile, compression and flexural moduli showed a gentle increase with the addition of increasing amounts of HA. The peak values were noted at 15 percent for tensile modulus and 25 percent for compressive and flexural moduli. It was recommended that the best compromise across all properties (mechanical and thermal) should be based upon the context of composite use. It was further recommended that PMMA/HA composite materials with 10 – 15 percent HA be investigated further, with due cognisance of the limitations of the present study.

The researcher recommended replication of the study using a larger sample size, more refined methodology and the incorporation of additional tests, including shear modulus testing, impact resistance, bioactivity and composite degradation.

DEDICATION

This study is dedicated to:

My parents, **Kun Quan Yang** and **Hong Di Liu**, who have been a pillar of strength and support throughout my life; and

My husband, **Graeme Kidson**, who has helped me through the many hours of testing, and has supported me with love through all the stages of this endeavour.

ACKNOWLEDGEMENTS

The author wishes to acknowledge and thank the following people and organisations who assisted in the implementation and reporting of this study:

Dr Ashley Ross, my supervisor, for his unerring direction and guidance, his endless editing capacity and for generally saving the day.

Professor Mark Walker, my co-supervisor, for his guidance in all matters mechanical and his massive editing prowess and encouragement

Dr Andre le Roux, for believing in my work so unfailingly, and for all his direction and encouragement.

My husband**, Graeme Kidson**, for assisting me in all the mechanical testing, and supporting me at all stages of the write-up.

The **Department of Mechanical Engineering** at the Durban University of Technology *[Steve Biko Campus]*, for the use of their laboratory and equipment during the testing phase of the study.

The **Department of Dental Technology** at the Durban University of Technology *[Steve Biko Campus]*, for the use of their laboratories and equipment to carry out this research study.

The **Postgraduate Development and Support Directorate** of the Durban University of Technology for their support and facilitation.

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DEFINITIONS OF TERMS

Bioactive material: A bioactive material is defined as one that elicits a specific biological response at the interface between it and the natural environment it is required to function in. This response must result in the formation of a bond between living tissues and the material (Shi, 2006).

Compressive modulus: Compressive modulus is defined as the stiffness (or resistance to shortening) of the material when loaded in compression. It is the gradient of the relationship between compressive strength and its corresponding compressive strain (the elongation divided by the original length) between two defined stress points. Thus

$$E_{compressive} = \sigma_j / \varepsilon_j$$

where:

$E_{compressive}$ = the elastic modulus in compression

σ_j = the compressive stress at sample point "j"

ε_j = the compressive strain at sample point "j"

(Ryder, 1973:3)

Compressive strength: Compressive strength is defined as the load applied to a material specimen (by squeezing it), divided by the cross sectional area. Thus

$$\sigma_{compressive} = L_{compressive} / A$$

where:

$\sigma_{compressive}$ = compressive strength

$L_{compressive}$ = maximum compressive load applied

A = the cross sectional area of the specimen at the point of failure

(Ryder, 1973:2)

Flexural modulus: Flexural modulus can be described as the resistance of a material specimen to bending. It is defined as the moment applied to a specimen, divided by the flexural stress at that point. The average gradient between two defined stress points is defined as the flexural modulus. Thus

$$Z_e = M_j / \sigma_{j\ flexural}$$

where:

Z_e = flexural modulus sample point

M_j = moment at sample point "j"

$\sigma_{j\ flexural}$ = flexural stress at sample point "j"

(Ryder, 1973:90)

Flexural strength: Flexural strength can be described as bending strength of a material specimen – how much force can be applied in bending. It is measured as the strength of a specimen supported at each end and loaded at mid point. It is defined as the moment applied to the specimen, multiplied by the distance of the application point from the specimen neutral axis and divided by its second moment of area. Thus

$$\sigma_{flexural} = My / I$$

where:

$\sigma_{flexural}$ = flexural strength

M = the moment applied to the test specimen by three point loading

y = the distance from the outermost surface of the test specimen to its neutral axis

I = the moment of inertia of the test specimen

(Ryder, 1973:88)

Methylmethacrylate: Methylmethacrylate is the liquid monomer component of the powder-liquid type of acrylic resin used to manufacture acrylic dentures (Craig 1997: 502).

Polymethylmethacrylate: Poly*methylmethacrylate* or PMMA is a chain polymer. It is a transparent acrylic resin, used as a denture base material, which exhibits outstanding clarity and is extremely stable (Craig 1997: 502).

Polymerisation: Polymerisation occurs through a series of chemical reactions by which a polymer is formed from large numbers of monomers to form a single large molecule of a high molecular weight (Craig 1997: 502).

Shear strength: Shear strength is defined as the resistance displayed by a specimen to failure when loaded by two opposing forces set apart by a minimal distance and acting through the thickness of a specimen. Thus

$$\tau = F / A$$

where:

τ = shear strength

F = the force applied through the thickness of the specimen

A = the shear area of the specimen

(Ryder, 1973:24)

Tensile strength: Tensile strength is defined as the load applied to a material specimen (by pulling it apart), divided by the cross sectional area. Thus

$$\sigma_{tensile} = L_{tensile} / A$$

where

$\sigma_{tensile}$ = tensile strength

$L_{tensile}$ = maximum tensile load applied

A = the cross sectional area of the specimen at the point of failure

(Ryder, 1973:2)

Transverse strength: The transverse strength of a material is obtained when one loads a simple beam, supported at each end, with a load applied in the middle. Such a test is called a three point bending test. The test determines not only the strength of the material, but also the amount of distortion expected. Transverse strength is often described as flexural strength (Craig 1997: 74).

Young's modulus: The elastic modulus in tension, (or Young's modulus), is defined as the stiffness, (or resistance to elongation) of the material when loaded in tension. It is the slope of the tensile strength to the corresponding strain (or elongation divided by original length) between two pre-defined stress points in the stress-strain curve. Thus

$$E = \sigma_j / \varepsilon_j$$

where:

E = Young's (or tensile) modulus

σ_j = stress at sample point "j"

ε_j = strain at sample point "j"

(Ryder, 1973:3)

CHAPTER ONE: THE INTRODUCTION

1.1 INTRODUCTION

Pure polymethylmethacrylate (PMMA), introduced in the 1960s by Charnley and Smith (Kim *et al.*, 2004), has been utilised as a replacement material for craniofacial repair. Materials suitable for this application should display the desirable properties of sufficient mechanical strength and promotion of bonding to existing bone if they are to be used for craniofacial replacement but PMMA promotes no bioactivity for good adherence to natural bone (Harper, Braden and Bonfield, 2000). It also demonstrates a very high exothermic polymerisation temperature which further hinders its use in the field of cranial replacement.

In recent years, there has been an increasing emphasis on the use of maxillofacial materials in a range of biomedical fields. In response to the demand for suitable prosthetic materials, hydroxyapatite (HA), since 1999, has been used in combination with PMMA as a an implant material that has demonstrated bioactivity, as well as some similarity in composition to natural bone (Itokawa *et al.*, 2007).

Previous researchers studying the PMMA/HA composite material have concentrated mainly on its bioactive properties (Zhang *et al.*, 2006). Somewhat lacking in the literature, thus far, has been a comparative analysis of the processing (thermal output) and mechanical properties of the range of percentage PMMA/HA composite combinations, as well as those of pure PMMA (Serbetci, Korkusu and Hasirci, 2003).

This study attempted to provide information on these properties, with a view to enhancing our appreciation of the scope and limitations of the possible clinical application of such PMMA/HA composites. It sought, firstly, to provide process data pertaining to the exothermic polymerisation cycle of the PMMA/HA

composites (thermal curing properties), in terms of the implication in the physical application of the composite to a repair zone. It also sought to refine the understanding of the effect of varying concentrations of HA within PMMA/HA composites, and its impact on the mechanical properties of the resultant composite. It was proposed that a more refined understanding of the relationship between the HA percentage and the resultant mechanical properties would aid in the improvement of use of PMMA/HA composites in reconstructive work and prosthetic design.

1.2 THE AIM OF THE STUDY

The aim of this study was to investigate the changes in exothermic polymerisation characteristics and a range of mechanical properties in PMMA/HA composites (of varying HA concentration) against a control sample of pure PMMA.

1.3 THE OBJECTIVES OF THE STUDY

The objectives of the study were to:

1. Investigate the exothermic polymerisation characteristics of a range of PMMA/HA composites (5% HA – 25% HA) against a control sample of pure PMMA;

2. Investigate the flexural maximum strength and modulus of a range of PMMA/HA composites (5% HA – 25% HA) against a control sample of pure PMMA;

3. Investigate the compressive maximum strength and modulus of a range of PMMA/HA composites (5% HA – 25% HA) against a control sample of pure PMMA;

4. Investigate the tensile maximum strength and modulus of a range of PMMA/HA composites (5% HA – 25% HA) against a control sample of pure PMMA; and to

5. Investigate the shear maximum strength of a range PMMA/HA composites (5% HA – 25% HA) against a control sample of pure PMMA.

The investigations described were conducted in each case, on five batches of specimens made from PMMA/HA composite, each with an HA percentage increasing in 5% increments from 5% to 25%, to those achieved by a control batch of pure PMMA.

1.4 THE ASSUMPTIONS

In this study, it was assumed that:

1. The number of specimens tested would be sufficient to indicate trends which could steer further research in a positive direction (if not providing data suitable for design purposes);

2. There would be sufficient homogeneity within the mixed material itself to preclude the effects of localised faults causing errors in strength and stress measurements;

3. The mixing homogeneity produced by the standard mixing process described was sufficient to ensure that property results were statistically accurate; and that

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

1.5 THE DELIMITATIONS

Arising from financial and other restrictions, the study was subject to the following delimitations:

1. In each parameter of mechanical property testing the maximum strength values and modulus values were measured and calculated. Due to the high costs of testing, and the budgetary restriction of the study, shear modulus testing was omitted from the battery of mechanical tests included in this study;

2. Any conclusions drawn from the results of this study would relate solely to the particular brand of PMMA/HA composite utilised in this study, prepared under similar methodology, and would not be extrapolated to all possible PMMA/HA composites, prepared under a range of methodologies;

3. Whilst the results of this study may provide considerations for the utilisation of PMMA/HA composites within certain clinical contexts, the necessarily limited scope of the study (in terms of sample size, range of tests and non-clinical context of testing) precludes the possibility of any firm recommendations and conclusions for the application of PMMA/HA composites, such as were tested in this study, in specific and defined clinical contexts.

CHAPTER TWO: THE REVIEW OF THE LITERATURE

2.1 INTRODUCTION

Medical research has been a focus of scientific development since ancient times. The human body is composed of such multifarious components, precisely designed and intricately composed, that it is hardly surprising that damage as a result of injury, disease or degradation is a common (if not inevitable) occurrence. Damage to bone, in particular, is most commonly caused by mechanical overload (broken bones), but also by diseases that influence the mineralisation of bone, or intrinsic destructive processes that either originate in the bone itself, or have spread from other parts of the body (metastasis).

It is self-evident that the bones of the human body have different purposes. Some, such as the bones of the arms and legs, have multiple functions: They anchor the muscles and provide a firm base for purposeful contraction, as well as providing protective sheathing for arteries, veins and nerves. They are also the structural frame that allows movement and load bearing through complex joint,muscle and tendon interaction. Other bones have the primary function of providing protection of soft internal structures, such as the ribs and the skull. The skull has a range of other functions which include, *inter alia*, the protection and housing of other vital structures such as the eyes and the cranial nerves, the ophthalmic muscles and cranial blood vessels. It also provides points of articulation with the jaw and teeth.

Teeth, in this respect, are themselves not immune to damage either. They are continually worn down through their lifetime; they are corrosively attacked by the environment in which they operate; they are sometimes broken through stress overload; and their surrounding tissues can become diseased.

The human skull is broadly composed of two principal structures: the cranium

and the mandible. The cranium is the larger part consisting, in the normal human, of 22 bones joined by semi-flexible sutures permitting almost no relative movement between them. Its function is the encapsulation of the brain and positioning of the eyes, ears and upper teeth, amongst others. The mandible is the lower jaw, which houses the teeth of the lower jaw and articulates with the cranium to allow for mastication, speech and facial expression.

There are many mechanisms for the repair of teeth, such as implants, crowns and dentures. The choice of mode of repair is determined by various factors, including the number of teeth that may be missing (or irreparably damaged) and the location of these within the mouth.

Implants are the preferred method when aesthetics are vital (such as in the fore part of the mouth), and these are biocompatible with both cranial and mandibular bone. Unfortunately, the techniques involved are very expensive and require higher standards of hygiene for the surgical premises than other less sophisticated methods. The patient's health status is also a consideration, and implant surgery is usually restricted to patients that are in otherwise good health. Crowns are usually used where the damaged or missing teeth cannot be seen easily. They are also expensive, but do not require the extreme hygiene standards required of implants, since their fitting require no invasive surgery. Dentures are, of course, prosthetics and, as such, are fabricated away from the patient, and fitted without any surgery whatsoever.

The materials utilised for the repair of teeth are extremely varied, and range from metals through ceramics to acrylics and polymers, and composites of all of the above. The focus on aesthetic considerations in the repair of teeth has increased markedly in modern times. This has resulted in an acceleration of the development of speciality alloys, intended for use as substrates for fused porcelain veneers.

Traditionally, the noble metals have been used for most types of restoration

because of their resistance to corrosion. Alloys of noble metals are used for the implant component of the porcelain replacement tooth. Almost all crown and bridge restorations consist of a porcelain fused to metal type repair, as this is well proven, robust and long lasting, and successfully maintains the original aesthetic of the human tooth and gum. The noble metals consist of ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold (in order of increasing atomic number). In the field of tooth repair, alloys of gold have been almost uniquely used for restoration. The high price of gold has meant that lower concentrations of it are used in the alloys used for repair work, but alternative materials are also being investigated. These are often categorised as 'gold-free', such has been the prevalence of gold alloys in the dental prosthetics industry.

2.2 DEVELOPMENT OF DENTAL MATERIALS

During the past forty years, polymethylmethacrylate has become the most popular choice of material for skull bone defect repairs (Velayudhan *et al.,* 2004). In the mid-1940s, PMMA was used to manufacture denture bases. Twenty years later, PMMA was used as a cranial defect reconstruction material (Jallot, 1998). In the quest to improve the performance of PMMA, it has at various times been reinforced with various additives, such as carbon fibre (Pal and Saha, 1982), graphite (Knoell, Maxwell and Bechtol, 1975), aramid (Saha and Pal, 1984), bone particles (Park, Liu and Lakes, 1986), polyethylene (Wagner and Cohn, 1989), titanium (Topolesk, Ducheyne and Cuckler, 1992), ultra-high molecular weight polyethylene (Pourdeyhimi and Wagner, 1989), PMMA fibers (Buckley, Gilbert and Lautenschlager, 1992), tricalcium phosphate (Yang *et al.*, 1997), and hydroxyapatite (HA) (Ishihara *et al.*, 1992).

Extensive work has been undertaken in attempting to combine the reinforcing materials listed above with PMMA, while preserving the twin ideal outcomes of sufficient mechanical properties (represented predominantly by PMMA) with

desirable biological properties (to varying degrees represented by the additives). Most of these material combinations have failed in one form or another (Yang *et al.*, 1999). In recent years, according to Shi (2006:8), HA has come to be seen as the most desirable material with which to combine PMMA in the creation of bone repair prostheses. The reasoning is simple: HA is a well-known biomaterial (Liu *et al.*, 1987). It is also the principal mineral found in both bone and teeth, with a chemical formula of $Ca_{10}(PO_4)_6(OH)_2$. It is known to be biocompatible, and, in a repair, is known to form a direct bond with neighboring bone material (Jallot, 1998).

Year	Development in Hydroxyapatite (HA) Application	Research advocates
1971	Use of HA as bone and tooth implant	More *et al.,*
1974	Use of HA as orthopedic implant	Hubbard.
1975	Use of HA for periodontal treatment	Nerf *et al.*,
1976	Development of processes for preparing dense polycrystalline HA	Jarcho *et al.*,
1977	Use of HA as loaded tooth roots in animals	Jarcho.
1978	Use of HA for Bonding to bone	Boyne & Shapton.
1979	Use of HA for dental root implants in Europe	Denissen & de Groot.
1980	Identification of the role of macro and microporosity in resorption rate and the biological response of HA	de Groot.
1980	Use of HA in alveolar ridge augmentation	Kent *et al.,*
1980	Use of HA to stimulate bone growth in porous metal implants	Ducheyne *et al.,*
1981	Use of HA to load tooth implants in Japan	Ogiso *et al.,*
1981	Use of HA in middle ear canal wall prostheses	Grote *et al.,*

Table 1: The evolution of the application of hydroxyapatite (HA) in prosthetic repair

In its pure form, HA is not an easy material with which to work. Shaping of the cured material during surgical procedures is not straightforward, and this makes

for some difficulty in creating properly-fitting prostheses. As a result of this, HA particles have been combined with PMMA to form various PMMA/HA composite materials. Lewis and Mladsi (1999) reported that the addition of HA (of up to 15 % by mass) to a PMMA-based bone cement resulted in an increase in the flexural modulus and fracture toughness when compared to pure PMMA. Daglilar and Erkan (2006) also found a decrease in the compressive strength of PMMA/HA when compared with pure PMMA. Jallot (1998) and Dalby *et al.* (1999) both reported that an increase in the amount of HA above the 15% threshold caused a decrease in the compressive strength of PMMA.

One of the main advantages of PMMA is its ease of fabrication and moulding into a wide variety of shapes (rod, film, fibre, sheet, etc.) . Advances in polymer chemistry have made it possible to tailor polymer properties for specific applications; this has been true also of PMMA (Daglilar and Erkan, 2006).

A typical PMMA material is supplied as a powder-liquid system. It consists of two parts: a solid component, presented as a powder and stored in a plastic packet, and a liquid component normally stored in a glass vial. The powder packet normally contains PMMA beads, 10% radiopaque barium sulphate (or sometimes, zirconium dioxide) and a small amount of benzoyl peroxide (normally 1%) as a polymerisation initiator (Anusavice, 1996). The glass vial contains the liquid MMA *[methylmethacrylate]* monomer and an activator (about 3% DMP toluidine) that promotes the curing process (Combe, 1986). The vial also contains a trace of a polymerisation inhibitor, such as hydroquinone, to prevent undesirable rates of polymerization, and to minimise spontaneous monomer polymerisation during storage.

When the two components are mixed (in the specified ratio) before use, the viscosity of the mixture gradually increases and becomes dough-like within a few minutes. This dough hardens in the next few minutes. This process involves MMA polymerisation. The filler powder in PMMA is used to minimise the shrinkage and the heat release caused by the polymerisation of the monomer

MMA. Without this, the pure MMA exhibits shrinkage of around 21 percent due to the change of density, and heat release which can increase the temperature to over 100℃ (Anusavice, 1996). In most commercial PMMA, when the powder part is mixed with the liquid part, polymerisation will occur spontaneously and will result in the formation of long-chain polymers that are essentially linear and relatively free of cross linking (Shi, 2006:7).

The curing (or polymerisation) process may be characterised by three easily differentiated stages, as cure completes. The first is known as 'dough time' and is defined as beginning with raw component mixing (PMMA with MMA) and ending at the point where the mixture will no longer stick to unpowdered surgical gloves (Anusavice, 1996). This occurs approximately two to three minutes after initiating the mixing process. During this period, the MMA wets and swells the PMMA beads and, simultaneously, polymerisation is initiated (Craig, Powers and Wataha, 1997).

'Working time' is considered to be the time from the end of 'dough time' up until the point at which the mixture becomes too stiff to manipulate, usually five to eight minutes. During this phase, the propagation of chain polymerisation continues and results in an increasing mixture viscosity (Anusavice, 1996). This persists until the mixture becomes hardened. The mixture can become very hot because the polymerisation process is an exothermic chemical reaction (Morrow, 1986). 'Setting time' is defined as the period measured from the beginning of component mixing until the surface temperature of the dough mass is one-half of its maximum value (Combe, 1986). It is as long as the sum of the dough time and the working time, and normally lasts between eight and ten minutes.

The clinical use of pure PMMA remains limited by several complications, most notably the observation that pure PMMA adheres insufficiently to bone surfaces as it possesses no bioactivity. This means that its bonding mechanics are limited to pure mechanical coupling. Curing PMMA also displays a very high

exothermic polymerisation temperature which is incompatible with the viability of biological tissues. Finally, it exhibits monomer toxicity (Kim *et al.*, 2004).

However, there are some virtues to the clinical application of pure PMMA: it is easy to mould into complex shapes, and is quick and simple to process. Because of these characteristics many researchers have attempted to modify PMMA in order to reduce the problems of bioactivity, exothermic polymerisation and monomer toxicity (Liacouras *et al.*, 2006) whilst preserving the desirable properties. A study by Ducheyne (1999) has shown that PMMA can be successfully utilised in combination with bioactive inorganic hydroxyapatite, or HA.

PMMA possesses mechanical properties that are suitable for the repair of natural bone. The Young's modulus value is between 1.8 - 3.1 GPa, compared to that of natural bone which is between 10 - 20GPa (Lewis and Mladis, 1999). This reduced modulus has been described as a positive feature when repairing natural bone, as it suggests that whilst PMMA may serve sufficiently as a replacement material, it would not have sufficient stiffness to support the entire load that the bone might normally carry. The result of this is that the body would not neglect the repair of the bone through its own methods, resulting on progressive strengthening of the repair with time (Fang, Gao and Leng, 2006).

The published range of tensile strength for pure PMMA is 48 - 76 MPa, with compressive strength performance being slightly better at 83 - 124 MPa (Jallot, 1998). These values again are similarly reduced, when compared with those of natural bone (Shi, 2006:7).

2.3 GENERAL INTRODUCTION TO COMPOSITES

A composite material is a single material consisting of two or more chemically

distinct constituents (on a macroscale), having a distinct interface separating them. In the field of replacement materials the PMMA/HA composite is a good example: it consists of PMMA as the primary matrix, and particulate HA as the dual purpose filling biomaterial. It is the most popular material for use in cranial replacement around the world (Montemartini, Cuadrado and Frontini, 1999).

In practice, most composite materials are designed to provide improved mechanical properties such as compressive, tensile, shear and flexural strengths and moduli. Therefore, they are frequently used as materials for orthopaedic applications where mechanical properties are a serious concern (Park, Liu and Lakes, 1986).

Much effort has been invested in the development of composite biomaterials for the repair or replacement of hard tissues. Besides the general consideration of biocompatibility, the specific consideration for bone replacement materials is of a biomechanical nature: the biomaterials should possess the mechanical properties necessary for a proper performance in the context of their function (Saha and Pal, 1984). According to Shi (2006:7), bone bonding properties often called bioactivity - have been demonstrated to be of great importance to in the evaluation of bone replacement materials.

The use of polymer matrix composites for bone replacement offers many advantages to both the surgeon and the patient in receipt of the prosthesis (Chow *et al.,* 2008). Not least of these is the opportunity it affords to avoid the problem of stress shielding, a problem encountered when using metal implants (of significantly higher-than-bone modulus) (Hench and Ethridge, 1982) in which the repaired bone is never given the opportunity to recover naturally over time, as it is never loaded fully. As a result, the prosthesis effectively carries all of the applied load. Composites can be tailored to more closely replicate the properties of natural bone (Hench, 1988).

Another advantage of the utilization of composites is the elimination of the need

for a second surgical procedure to remove the prosthetic implant if the implant is able to be made biodegradable (Hench, 1988). Such utilization would also eliminate the ion-release problem associated with metal implants. The possibility of making composites only as strong as cortical bone, and to improve the material's bioactivity, or bone bonding activity, by adding a secondary reinforcing phase makes the pursuit of a composite alternative very attractive. In this regard, fibres and ceramic filler particles have been used to reinforce the polymer materials, whilst simultaneously improving the bone bonding bioactive properties of the composite (Buckley, Gilbert and Lautenschlager, 1992).

2.3.1 PROPERTIES OF HYDROXYAPATITE

Bioactive hydroxyapatite or HA has been extensively studied due to its propensity for bonding with natural bone. HA has been used successfully in clinical applications for more than 20 years due, in part, to its chemical similarity with the mineral components of bone and other hard tissue in mammals (Kim *et al.*, 2004). For example, it includes in its construction the same ions that are present as mineral components in teeth and bones (Shi, 2006:8). It shows excellent biocompatibility not only with hard tissues, but also with soft tissues, such as skin and muscle and has played a key role in the calcification and resorption processes of bone (Kim *et al.*, 2004). HA also exhibits good biological stability and affinity and it is because of these properties that a number of researchers (Shi, 2006:8; Jallot, 1998; Liacouras *et al.*, 2006), such as Jarcho *et al.* in the USA, de Groot *et al.* in Europe, and Aoki *et al.* in Japan, in the 1970s worked towards the development and commercialisation of HA as a biomaterial for bone repair, augmentation and substitution.

The methods of processing HA can be classified into two categories: dry processing, (powder), and wet processing, (bulk), chemical methods. This categorization depends on the aqueous solvent used. As a result of its good tissue response, HA has been routinely used in orthopedic surgery in both powder and bulk forms. However, both forms display insufficient mechanical

properties, and this precludes their use in load-bearing situations. In fact, the physical weakness displayed by pure HA has been the primary obstacle to its successful application in hard tissue prosthetics. The best solution to this problem has been to use HA as a reinforcing material in a composite which provides the mechanical properties required. Various methods have been developed such as using HA as the reinforcing ingredient in metals or PMMA composites (Castaldini and Cavallini, 1985).

Cured HA exhibits complete stability when in contact with aqueous media, such as body fluids, at the human body's ambient temperature of 37℃ (Anusavic, 1996). HA is bioactive and promotes osteointegration when directly implanted into bone. The main components of natural bone tissue are calcium phosphate (69% by mass), water (10% by mass), collagen (20% by mass), with other organic materials making up the remainder (1% by mass) (Shi, 2006:8). These include, in small quantities, proteins, polysaccharides (structural tissues) and lipids (energy storage). Calcium phosphate is present in the form of crystalised HA and amorphous calcium phosphate. Its main function is to provide structural stiffness to the bone tissue. In the human body the most important calcium phosphate is HA with a Calcium:Phosphorus (Ca:P) ratio of 5:3 (Zhao *et al.*, 2005).

The value of the mechanical properties measured for HA depends strongly on the porosity, grain size and impurity quantity present in an HA sample (Wang *et al.*, 2005). Further to this, the method utilised for measuring the mechanical properties may strongly influence the end results – there are a range of methods and standards that have been used in previous studies making like-for-like comparisons between researchers difficult. In view of these factors, the values presented in this study can only be used for comparative purposes within the context of this specific study, and should not be extrapolated to other studies or be used for design purposes.

The published values of Young's modulus for dense HA materials are typically

much higher than those of hard tissue: the Young's modulus of HA falls within the (broad) range of 35 - 120 GPa, while for hard tissue the value is 10 - 20 GPa. The bending strength, compressive strength and tensile strength of the dense HA are, respectively, in the ranges of 38 - 250 MPa, 120 - 900 MPa, and 38 - 300 MPa, which are comparable to that of hard tissue (Jallot, 1998). However, from the perspective of the safety of biomedical implants, the mechanical properties of dense HA are not good sufficient for load-bearing applications mostly because HA materials have low fracture toughness values (K) meaning that crack propagation in HA components is likely. Pure HA also exhibits a poor Weibull modulus value of between 5 – 113. This indicates a lack of homogeneity in the flaw distribution of HA components, reducing the margin of safety in the structural design. These two negative properties are typical of a brittle ceramic, showing high susceptibility to crack growth and poor behaviour reliability under load (Shi, 2006:21). By way of example, Shi (2006:21) found that most of the loaded dental HA implants used in his study were broken within one year.

Zhao *et al.* (2005) confirm that pure HA suffers from insufficient fracture toughness irrespective of its structural qualities; whether dense or porous, pure HA allowed excessive crack propagation. Composite materials composed of HA with PMMA were developed to improve on the mechanical property benchmarks set by HA (Wang *et al.*, 2002).

2.3.2 POLYMETHYLMETHACRYLATE/HYDROXYAPATITE COMPOSITES

Generally the process of partial skull replacement has a high success rate, but failure of the prosthesis can occur. These failures are mainly due to aseptic loosening which is often caused by the failure of the material mantle (Taylor *et al.*, 2004). A good interface between the replacement prosthesis and original bone is crucial. The replacement needs to show excellent biocompatibility not only with hard tissues, but also with soft tissues, such as skin and muscle.

Studies by Schmitz, Hollinger and Milam (1999) have been conducted on bioactive composite materials. It has already been stated that PMMA is the most widely used of the available materials in the fields of maxillofacial and orthopaedic reconstructive surgery, primarily because of their ease of manufacture (Serbetci *et al.*, 2003). However Harper *et al.*, (2000) highlight that PMMA does not possess the bioactivity characteristics ideally required of an implanted prosthetic material.

Added to this, PMMA is typically mixed in surgery and then inserted into the bone cavity and the cure cycle is completed *in vivo*. Due to the high temperatures released during the exothermic polymerisation curing cycle and the inherent toxicity of the MMA monomer component, bone necrosis can occur. As a consequence of this a fibrous encapsulation layer is formed around the implant (including between the natural bone and the implant) which allows micromotion to occur. This can cause pain to the patient, but, more significantly, creates a space for particulate wear to exacerbate over time (Ho and Marcolongo, 2005). A solution to this problem at the prosthetic interface is to use bioactive ingredients in the creation of the composite repair material (Ducheyne, 1999).

Currently, most commercially available skull replacement materials are based on PMMA. A variety of filler particles have been used for increased bioactivity including HA; natural bone particles, and even growth hormone has been added as a bioactive filler (Ducheyne, 1999).

According to Velayudhan *et al.* (2004), the brittleness and non-workability of HA limits its clinical application as a cranioplastic repair material. Pezzotti and Asmus (2000) further state that HA displays poor fracture characteristics is therefore of limited use as a skull replacement material. Zhao *et al.* (2005) confirm that both dense and porous HA suffer from insufficient fracture toughness.

Investigations undertaken by Ducheyne (1999), Liacouras *et al.* (2006) and Wang *et al.* (2005) were primarily concerned with *in-vitro* evaluations of the bonding of PMMA with HA. These investigations show that the PMMA/HA composite material has good bioactivity when compared with pure PMMA. In such situations, silane is introduced to further improve the bonding between the PMMA and HA (Harper *et al.*, 2000) since silane is commonly used to improve the bonding between polymer based matrices and reinforcing filler materials such as fibreglass.

In recent years, composite materials consisting of bioactive inorganic HA particles and organic PMMA particles have been extensively studied (Wang *et al.*, 2002). Daglilar and Erkan (2006) have shown that PMMA/HA has improved bioactivity compared with PMMA. Unfortunately the influence of the HA filler on the mechanical properties of PMMA/HA composites has not been studied sufficiently to determine, or even suggest an optimum PMMA/HA mixing ratio (Serbetci *et al.*, 2003).

Daglilar and Erkan (2006) have further observed that HA acted as a rigid filler material in the composite, enhancing flexural strength. According to Velayudhan *et al.* (2004), the addition of up to 15% HA (by weight) to PMMA resulted in an increase in the flexural strength compared to PMMA alone. In addition of up to 25% HA improved the flexural properties of the composite. Wang *et al.* (2005), demonstrated that beyond 25% HA the mechanical properties start to decrease, because the addition of HA increased the material porosity and resulted in a general decrease in the mechanical properties of material.

2.4 CONCLUSION

From the review of the literature it would are appear that the mechanical characteristics of PMMA/HA composites are dependent upon the amount of HA added to the composite (Serbetci *et al.*, 2003). The addition of small amounts

of HA into PMMA appears to offer the possibility of strengthening or stiffening the composite without adversely affecting stress distribution, or causing processing problems due to increased viscosity. It has an effect on the mechanical properties and the exothermic polymerisation but does not affect the curing time (Taylor *et al.*, 2004).

PMMA/HA composites further display improved mechanical properties than either of the base constituents alone. The composites display an apparent transition point in their performance: When the HA percentage is lower than this point, the composite displays superior strength and suitable Young's modulus for bone replacement (Serbetci *et al.*, 2003). Of critical importance however, is the observation that when the HA percentage is above this point, the mechanical virtues seem to decrease abruptly. All composites demonstrate low bioactivity in inverse relationship to their HA concentration.

Understanding the changing mechanical characteristics of the PMMA/HA composite, as the HA percentage increases is therefore of critical importance for the successful exploitation of such composites as replacement materials within a clinical context. Their potential for use *in vitro* is also related to the temperature generated during curing.

This study therefore seeks to characterise the exothermic polymerisation behavior (curing properties) and the mechanical property variations of PMMA/HA composites with a range of HA percentages in order to shed light on the potential for future clinical applications.

CHAPTER THREE: THE MATERIALS AND METHODS

3.1 INTRODUCTION

The methodology employed in this study sought to characterise the effect of the component ratio of polymethylmethacrylate/hydroxyapatite (PMMA/HA) composites in terms of inherent exothermic behaviour during cure, as well as their mechanical properties (these being strengths and moduli for various loading regimes). This methodology involved two components:

1. An experimental component that provided data on the exothermic polymerisation characteristics of each PMMA/HA composite; and
2. An experimental component that provided data on flexural, compressive, tensile and shear properties of the respective PMMA/HA composite.

3.2 THE MATERIALS EMPLOYED IN THE STUDY

Polymethylmethacrylate (PMMA) is an acrylic resin capable of providing sufficient mechanical strength for the repair of bone defects and is commonly used to repair the skull (Serbetci *et al.*, 2003). An identified weakness of the use of PMMA in these contexts is that PMMA shows no bioactivity and exhibits high exothermic polymerisation temperatures (thermal curing properties). The use of hydroxyapatite (HA) as a repair material is limited in its clinical application because of its brittle nature, poor malleability and poor fracture characteristics (Shi, 2006:8). Accordingly, in order to maximise on the desirable mechanical properties of both PMMA and HA, composite materials, composed of various ratios of PMMA and HA have been developed. According to Itokwa *et al*. (2007), PMMA and HA are the most commonly used materials for cranioplasty.

In the previous chapter it was illustrated that there is a paucity of information available on the specific effects of varying the quantity of HA in PMMA/HA composites. Therefore, this study focused on identifying the effects of such variation on the mechanical properties and curing characteristics of a range of PMMA/HA composites.

From a strictly mechanical perspective, the role of PMMA within the context of a composite is that of any polymer and serves as the matrix, with HA serving as a filler material that decreases the cure shrinkage, bulks the composite and reinforces the matrix (Zebarjad *et al.,* 2011). From a biological perspective, the HA also adds the property of bioactivity to the composite.

The materials sourced for this study include:

- Hydroxyapatite powder (HA) Calcium/Phosphorus = 1.67; density = 3.16g/cm^3; size grade 50-150µm (Wuhan University, People's Republic of China)
- Polymethylmethacrylate (PMMA) size grade 50-75µm; and methyl-methacrylate (MMA) monomer (Coral Chemistry Factory of Shanghai, People's Republic of China).

3.2.1 THE FORMULATION OF THE COMPOSITE MATERIALS

The two components of the composite, as described above, were mixed in accordance with instructions recommended by Lewis and Mladsi (1999). The respective weighed quantities of PMMA and HA (as measured by analytical balance with a resolution of 0.1mg) are shown in ***Table 3***, below.

The solid components of the PMMA/HA composite were mixed for three minutes, using a non-aerating mixer set at 60rpm. The aim was to achieve a homogenous component distribution. The mixed dry constituents were kept in a clean, dry, air-tight, inert, opaque container. Both solid and liquid components

were kept at a controlled temperature of 21±1˚C for a minimum of 48 hours prior to being mixed. The mixing procedures were carried out in the Mechanical Engineering Prototyping Research Laboratory at the Durban University of Technology (DUT).

The materials required by each sample batch were prepared in the identical manner, and mixed in terms of the Lewis and Mladsi recommendations (1999), as cited above.

3.2.2 SPECIMEN IDENTIFICATION

Specimens were divided into groups according to HA concentration. All groups were given the prefix “G” followed by the HA percentage (from 0 to 25). The next letter in the coding sequence denoted the type of test performed [E *(exothermic)*, T *(tensile)*, C *(compressive)*, S *(shear)* or F *(flexural)*]. A final number affixed to the code denoted the sample number (from 1 to 5). By way of illustration, G5E3 indicates a 5%HA (G5), exothermic polymerisation test (E), specimen three (3) of five.

Table 2, below, summarises the names given to the 30 specimens (across the six HA concentration groups) tested specifically for their exothermic polymerisation characteristics.

Sampling sequence	EXOTHERMIC GROUP DESIGNATOR					
	G0E	**G5E**	**G10E**	**G15E**	**G20E**	**G25E**
1	G0E1	G5E1	G10E1	G15E1	G20E1	G25E1
2	G0E2	G5E2	G10E2	G15E2	G20E2	G25E2
3	G0E3	G5E3	G10E3	G15E3	G20E3	G25E3
4	G0E4	G5E4	G10E4	G15E4	G20E4	G25E4
5	G0E5	G5E5	G10E5	G15E5	G20E5	G25E5

Table 2: The designation of samples within the exothermic polymerisation test

3.2.3 THE PREPARATION OF PMMA/HA COMPOSITES FOR EXOTHERMIC POLYMERISATION TESTING

The sample size for this test was limited by financial constraints and set at five samples per test batch (at each incremental increase in HA percentage). It was hoped, however that the small sample size selected would satisfy the relevant testing standards at least for comparative purposes if not for definitive characterisation. Six specimen groups were identified with varying percentages of HA from zero percent to 25 percent. The group containing zero percent HA was used as the 'control group, and the upper limit of 25 percent HA (by mass) was selected as the practical upper limit for popular use of the PMMA/HA composite.

GROUP	PERCENTAGE *(by mass)*		ACTUAL MASS *(g)*		TOTAL MASS *(g)*
	PMMA	HA	PMMA	HA	
G0	100	0	150.00	0.00	150.00
G5	95	5	142.50	7.50	150.00
G10	90	10	135.00	15.00	150.00
G15	85	15	127.50	22.50	150.00
G20	80	20	120.50	30.00	150.00
G25	75	25	112.50	37.50	150.00

Table 3: The relative masses of PMMA and HA employed in the preparation of the exothermic polymerisation test samples.

The composite components for each sample were mixed as per Section 3.2 *(above)*. Once mixed, each specimen was formed by hand rolling into a sphere of 25mm diameter, which was checked for geometrical consistency using a hemispherical checking gauge. This promoted consistent test results by creating equivalent conditions for the determination of heat lost through surface area radiation versus the heat generated by the chosen geometry for the fixed volume. As the study was fundamentally comparative, the defined volume was

selected as being small enough to be both easily handled and unlikely to be self-damaging through self-ignition, yet large enough to enclose the thermocouple of the temperature testing equipment completely.

3.2.4 THE PREPARATION OF PMMA/HA COMPOSITES FOR MECHANICAL STRENGTH TESTING

The composite materials utilised in the mechanical strength tests were prepared according to the methodology described above. Mechanical property determination is usually performed in compliance with the appropriate standards, as published by an authoritative organisation such as the South African Bureau of Standards (SABS), in South Africa, or, internationally, the International Standards Organisation (ISO), the American Standard Testing Method (ASTM), the British Standard (BS) and others (Kim *et al.*, 2004).

Standards are followed in order that comparative studies between materials are able to be made, in the knowledge that independent variables applied during a particular test will have been applied in a comparable test in the same manner, irrespective of the place or time of testing. This means that if two materials are tested utilising the same standard, a direct comparison can be made between them.

The material being tested normally determines the choice of standard to be applied, because what may constitute an appropriate standard for one material may not be appropriate to another. An example would be the determination of rate of strain: some materials (such as rubber) may be strained at a very high (even instantaneous) rate without affecting their strength, whilst others, such as most rigid plastics, will elongate if strained slowly but will snap at a lower stress if strained excessively rapidly. It is therefore of critical importance that an appropriate standard for the material being tested is selected.

PMMA and PMMA/HA composites are orthotropic, non-fibre-reinforced

polymers. The addition of HA qualifies the polymer as 'filled'. Testing standards applicable to this type of material were identified and applied to each of the following tests as per ***Table 4***, below.

MECHANICAL TEST	STANDARD
Flexural strength and modulus	ISO 178
Compressive strength and modulus	ISO 604
Tensile strength and modulus	ISO 527-4
Shear strength	ASTM D 5379

Table 4: The mechanical test standards

Whilst standards particular to the determination of the mechanical properties of PMMA have been developed and published (*viz.* ISO 5833:2002 and ASTM F451-99a), these were not utilised due to the financial limitations of the study *[see Section 1.5, above]*. The standards selected are appropriate to the classification of the material and are therefore relevant, despite being general rather than specific to PMMA. Since this study was focussed on the composite material *per se*, rather than its application in specified clinical contexts, it was decided, further, to apply existing materials standards in favour of existing standards for polymers in specific clinical contexts e.g. the ISO5833 and ASTM F451-99a, for polymers as bone cements (Demian and McDermott, 1998).

The standard for each type of test performed (flexural, compressive, tensile and shear) specifies the geometry required for each specimen. As such, four differently shaped dies were made from 316 grade stainless steel. The respective die geometries were drawn using a computer aided design (CAD) package and stainless steel sheets of the correct thickness were sourced and laser cut to suit.

It was found that the laser cutting method left an unacceptably rough edge consisting of repeated transverse ridges along the edges of the dies.

Specimens made with such dies were unusable, as the ridges were found to influence the test results through stress raisers. Measurement of the dies also found them to by rendered oversize by the thickness of the ridges. It was found that a simple abrasive polishing process corrected both the rough edges and the size non-conformance simultaneously. The smoothing of the die edges rendered smooth-edged moulds for use in the flask and packing procedure applied in the manufacture of the test specimens.

The flask and packing method involved placing the stainless steel dies on the centre-line of a split metallic container or flask. One half was filled with a bespoke casting plaster and allowed to set. This casting was then released and the other half poured in the same manner. When the die was removed a female cavity mould was produced. The specimen dies are shown in ***Figure 1*** *(below)*.

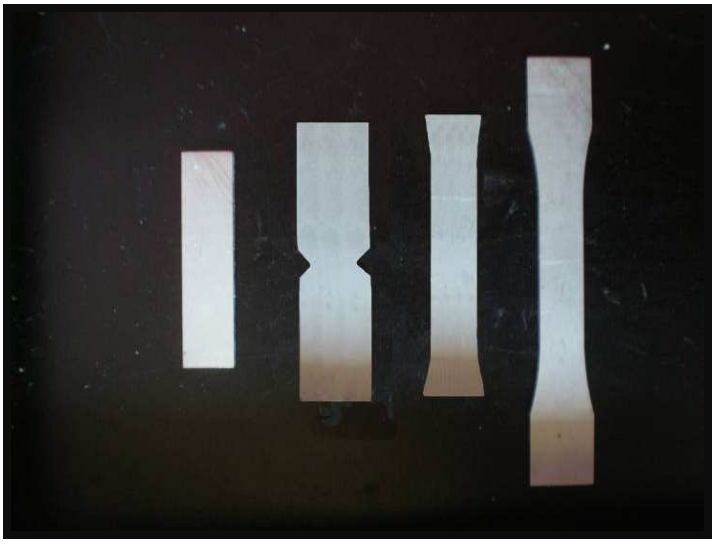


Figure 1: The stainless steel dies used in the specimen manufacture for the following tests: (from left to right), flexural, shear, compressive and tensile strengths and moduli

The design of the dies incorporated a compensation factor for the inherent shrinkage of the polymer during the curing process. This allowed the specimens to follow more accurately the dimensional requirements of the

testing standards. Before the dies were designed the shrinkage of the material was determined experimentally by producing a rectilinear sample in a mould of known dimensions. It was found that the polymerisation process resulted in shrinkage (in three dimensions) of two percent. As such each die was created with a two percent length increase in its three planes so that the specimens would be produced to the required specification. This attention to detail, in retrospect, was perhaps unnecessary as the outcomes of all of the tests use the cross sectional area of the specimens in the calculations and deviations are therefore accounted for, but since it was understood to be a simple procedure to realise dimensionally "correct" specimens, it was done. Every specimen (for each respective test) was manufactured using the same die, thereby minimising variation in the geometrical form of each specimen. This strategy was aimed at improving the repeatability of the results by removing the geometrical variable in all three planes. Despite the conservative approach adopted in the rendering of specimens of each type, every specimen was individually measured and its specific dimensions used to calculate the properties specific to it.

3.2.4.1 The Specimen Manufacturing Procedure

Specimen material was mixed according to the methodology described in Section 3.2 *(above)* and the homogeneous dough obtained was quickly but carefully placed into the pre-prepared mould, as in the study by Serbetci *et al.* (2003), described above.

The moulds were flasked and packed with a controlled volume of activated PMMA or PMMA/HA mix. They were then placed in a hydraulic press and closed slowly with incrementally increasing force. The specimens were made by packing the correct volume of catalysed PMMA/HA into the flask and then clamping down so that the flask closed completely, ensuring that the geometry and dimensions of the specimen being produced were preserved. The pressure was maintained throughout the processing and curing cycles (Kim *et al.,*

2004). The processing and curing processes were completed in ambient laboratory conditions (set at 21 ± 1˚C) (Lewis and Mladsi, 1999).

After curing, each specimen was removed from the mould and it was found that each specimen required a minor clean-up operation to remove the very thin flash produced by the moulding process. Such operation was in conformance to the requirements of specimen preparation described in the standards, and conventional methods were employed: the flash was removed by means of a cutting operation using a new, high speed steel four flute end mill driven by a CNC *[Computer Numeric Controlled]* milling machine (as illustrated in ***Figure 2***, below) with an accuracy of 0.05 mm. The machine was set at a very high feed rate (of 3m/min) to ensure that as little heat as possible was transferred to the specimen being trimmed. Water mist cooling was used as an extra precaution against introducing extraneous heat, and thus altering the extent of polymerisation.

A great deal of care was taken to preserve the geometrical form, particularly the edge and corner geometry, as any variation of these features would affect the reliability of test results.

Figure 2: The Multicam® CNC milling machine at DUT

After the trimming operation was completed, the specimens were polished with increasingly fine polishing paper, starting with P800 and ending with P3000 (800 to 3000 abrasive particles per square inch). This was to remove any residual machining marks left by the milling operation. The polishing paper was glued onto flat sheets of glass to ensure that no corruption of the specimen geometry was possible. All specimens were sanded until they displayed smooth and highly polished surfaces. Care was taken to sand consistently in the same plane and direction of the intended strain, as per the respective testing standard specification. All of the above precautions and methods guarded against the introduction of any geometrical stress raisers that might affect test results.

The six sample groups, which are shown in ***Figure 3***, were measured utilising a Mitutoyo® vernier calliper (of 0.05mm maximum resolution) for length and breadth. A Mitutoyo® micrometer (of 0.01mm maximum resolution) was used to measure specimen thickness. A flat anvil was used to measure the individual specimens, the surfaces being judged suitably uniform for flat anvil measurement. Averaging of three individual measurements of thickness along the length of each specimen was performed, confirming that the uniformity of the thickness was within the tolerance prescribed by the respective testing standard. All measurements were taken in the laboratory that contained the testing equipment, and specimen had been allowed to acclimatise for 12 hours prior to measuring.

As proposed by Zhao *et al.* (2005), the specimens were stored in distilled water at a temperature of 37˚C for two weeks before testing commenced. A digitally controlled Binder oven, as shown in ***Figure 4*** *[overleaf]*, at the Department of Mechanical Engineering was used to keep each specimen in a controlled environment right up to the initiation of mechanical property testing.

Figure 3: 120 specimens from top to bottom, the six groups (G0 to G25) and from left to right, five specimens each for flexural, compressive, shear and tensile testing.

Figure 4: The Binder oven kept the specimens at a constant 37˚C in distilled water

A schedule of flexural, compressive, tensile and shear strength tests were then performed, at the Department of Mechanical Engineering, utilising a LIoyd® LR30K universal testing machine, as illustrated in ***Figure 5***. The machine was fitted with the appropriate testing attachments required by the relevant standard. This included a three point bending rig, tensile grips, and bespoke compression and shear apparatus. Data was produced in digital form.

Load was measured by the smallest capacity (1000N) load cell available, in order to maximise resolution. This load cell was certified accurate up to 95 percent of its maximum capacity, or 50N, thereby fulfilling the standard accuracy requirements with a minimum load value of 50N. Extension was measured using an external extensometer, free from the effects of strain on the machine itself. An extensometer of 5% strain capacity (or 2.5% on either side of the zero strain mark) was selected, again in the interests of maximising resolution. The testing machine itself was located in an air conditioned room at constant temperature and humidity.

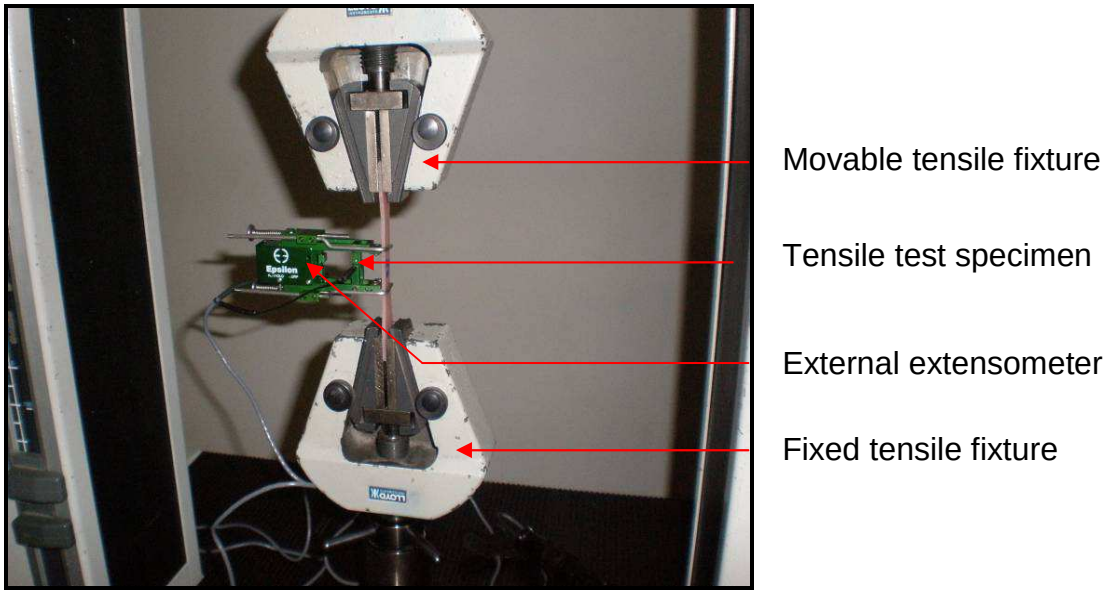


Figure 5: A tensile test being carried out using the LIoyd® LR30K universal testing machine.

3.3 THE METHODS EMPLOYED IN THE STUDY

3.3.1 THE EXOTHERMIC POLYMERISATION TEMPERATURE TESTING (EPT TEST)

The temperature measuring station of a Heatcon® 2000 Hot Bonding machine was used to test the specimens for exothermic temperature change. This station too was located at the Mechanical Engineering Department at DUT, and is illustrated in ***Figure 6***, below.

Figure 6: Heatcon® 2000 hot bonding machine

The ambient test environment was controlled by means of air conditioning, and was set at 21±1℃. A j-type thermocouple temperatur e sensor was carefully inserted into the centre of each spherically-shaped specimen immediately after the completion of the mixing process and before the exothermic reaction could start (during what has been described previously as the 'dough' stage). The temperature data was recorded at a fixed time-based sample rate as the specimen cured. The recorded temperatures were then plotted against time to determine both the exothermic gradient as well as the peak exothermic temperature.

3.3.2 THE MECHANICAL STRENGTH TESTS

3.3.2.1 The Flexural Strength and Modulus Tests

As indicated in ***Table 4*** *[See Section 3.2.4, above]*, the Standard ISO 178 was selected as the most suitable for testing the PMMA/HA composite material under flexural conditions. The scope of the particular standard specifies the testing of unreinforced and filled plastics in flexure, to determine their maximum flexural strength and flexural modulus.

It is important to note that the flexural modulus is not directly comparable with Young's modulus (or tensile modulus). This is due to the shear effects present when testing by bending which act as an additional destructive element with which the material must cope. Consequently it is expected that the modulus in flexure will be reduced when compared with Young's modulus. The shear effects are minimised by defining the relationship between the specimen bearing length and thickness. This is clearly stated in the ISO 178 standard, and is indicated to be set at not less than 15:1.

The flexural testing apparatus was set up using a vernier caliper to set the required span length. The span supports were compliant with the requirement of a two millimetre radius. The loading member had a radius of five millimetres, as specified. It was ensured that the axes of the three members were parallel and that the loading member was centrally located with reference to the span supports. A single sacrificial test specimen was tested to ensure that localised crushing at any of the members was not occurring and when this was confirmed, formal testing was effected. The specimen geometry is detailed in ***Figure 7***, below.

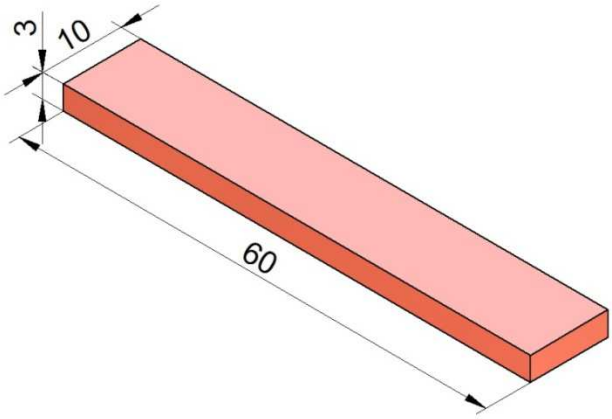


Figure 7: Flexural strength and modulus tests specimen geometry (mm)

Each test specimen was supported as a beam with span supports inboard of its ends, as specified by the standard. The load was applied such that the specimen was deflected downward. The deflection was allowed to continue at a constant rate of 2mm/min (giving a strain rate of 0.01mm/mm/minute) until failure occurred.

Deflection was measured by means of a Mitutoyo® linear displacement gauge, centrally located between the beam supports and with its measurement axis parallel with the direction of deflection. The gauge was graduated in 1/100ths of a millimetre and added negligible resistance to the deflection of the beam. A representation of the flexural test setup is shown as ***Figure 8***, below.

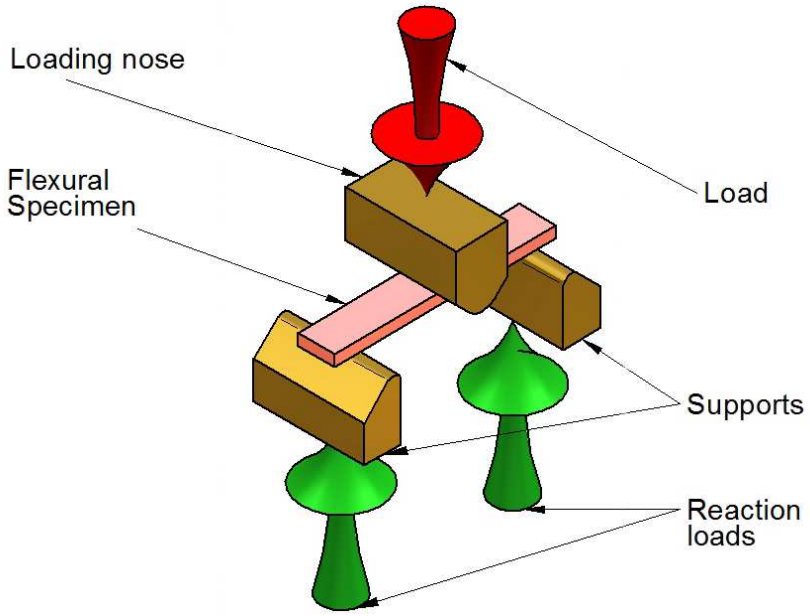


Figure 8: Flexural strength and modulus tests setup

3.3.2.2 Compressive Strength and Modulus Tests

The standard selected for the compressive strength and modulus tests was ISO 604, described as suitable for filled, rigid thermoset moulding compounds. Specimen preparation was completed in conformation with the standard and is detailed in Section 3.2.4.1, above. The tests were performed using the Lloyd® LR30K universal testing machine, operating in compressive mode. For these tests a load cell with a maximum load capacity of 1kN was selected. Strain was measured using an Epsilon external strain gauge, with the gauge length of the extensometer set at 23 millimetres.

In testing the specimens, great care was taken to load the specimens in the testing grips in such a manner as to ensure that their longitudinal or major axes were parallel with the direction of strain. The bending and shear effects of skew-loaded specimens were avoided, as far as possible, by means of accurate alignment through careful measurement by means of vernier calipers.

The testing grips consisted of a pair of self-tightening jaws: one rigidly mounted to the table of the tester; the other mounted to the crosshead of the tester through the load cell. The grips were provisionally tightened by hand as the 'pre-load' component of the tensile test. This pre-load was added to the load to which the specimens are subjected when calculations were performed.

The specimen geometry chosen was type 1B, the 'dog bone' type. The geometry, in compliance with the standard requirements, is shown in ***Figure 9***, below.

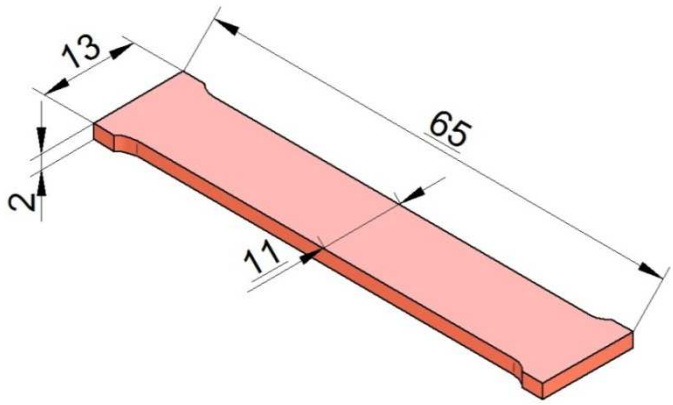


Figure 9: Compressive strength and modulus tests specimen geometry (mm)

The rate of separation was set at two millimetres per minute. Measurement of elongation (in µm) and load (in N) was set at 100 sample points. A representation of the test setup is shown as ***Figure 10***, below.

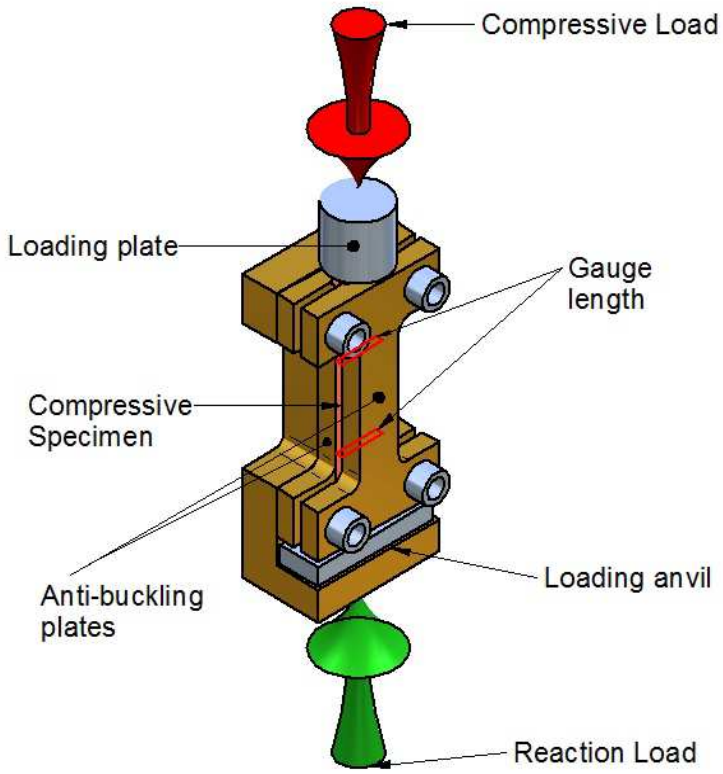


Figure 10: Compressive strength and modulus tests setup

3.3.2.3 Tensile Strength and Modulus Tests

The standard selected for the tensile strength and modulus tests was ISO 527-4. Specimen preparation was completed in conformation with the standard detailed in Section 3.2.4, above. The tests were performed utilising the Lloyd® LR30K universal testing machine operating in tensile mode.

The specimens were tested along their longitudinal axis, referred to in ISO 527-4 as Axis 1. Great care was taken to load the specimens in the testing grips in such a manner as to ensure that they were parallel to the axis of strain. The bending effects of skew-loaded specimens were thus avoided. Alignment was achieved, as far as possible, by measurement with vernier calipers. The specimen geometry chosen was again type 1B, the 'dog bone' type, and such geometry, compliant with standard requirements, is shown in ***Figure 11*** below.

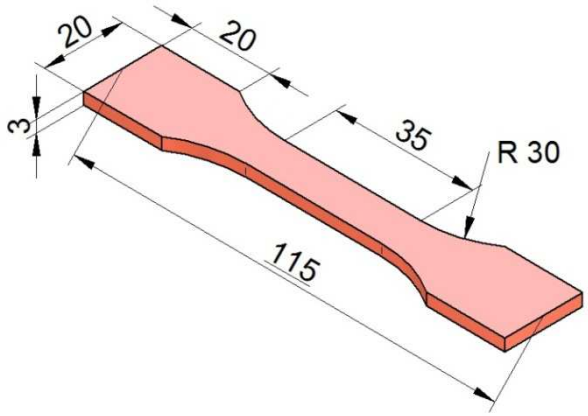


Figure 11: Tensile strength and modulus tests specimen geometry (mm)

The rate of separation was set at two millimetres per minute. Measurement of elongation (in µm) and load (in N) was set at 100 sample points. A diagram detailing the tensile test setup is shown as ***Figure 12***, below.

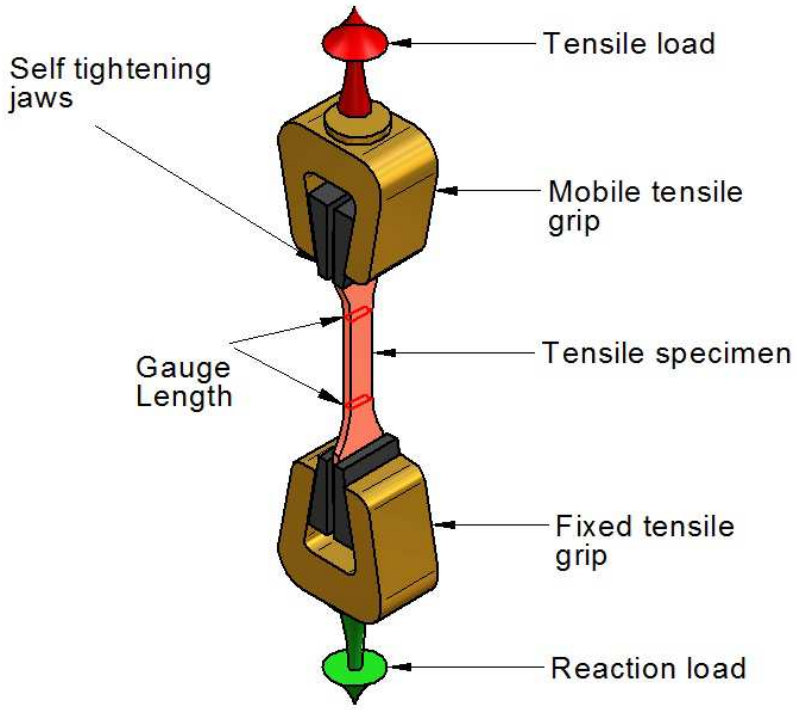


Figure 12: Tensile strength and modulus tests setup

3.3.2.4 Shear Strength Test

The determination of the shear strength of the various PMMA/HA combinations was conducted according to the specifications laid down in the standard ASTM D5379. The scope of this standard confirms it to be suitable for the evaluation of shear strength and shear modulus of isotropic rigid materials such as the filled, rigid polymer being tested in this study.

The test was conducted utilising the Lloyd® LR-30K universal testing machine operating in tensile mode. Specimens were prepared in conformity to the standard.

The test specimens were measured in thickness with a micrometer having a resolution capacity of 0.01mm, and in length by vernier calipers with a resolution capacity of 0.05mm.

The dimension across the V-notches was also measured by means of the vernier calipers. The mean dimensions were recorded, and used for calculations. The spread of results when measuring the specimen dimensions was acceptable. The dimensions of the ±45° notch including the radii at the vertices were also confirmed during the test procedure. The specimen geometry is shown in ***Figure 13***, below.

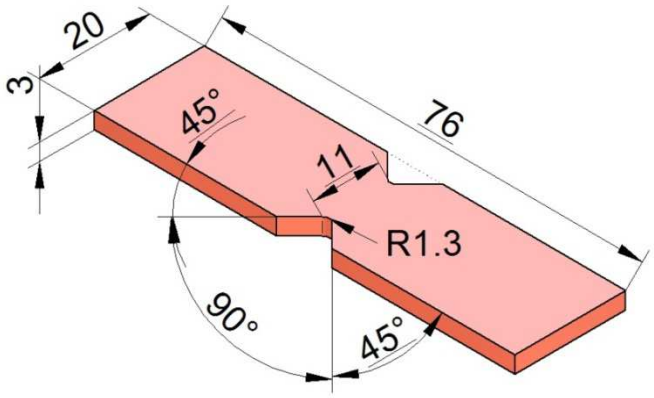


Figure 13: Shear strength and modulus tests specimen geometry (mm)

The specimens were loaded in the V-notch shear testing fixture. Self-alignment systems for the specimens integrated into the jig ensured that the specimens were aligned with their major surface parallel with the direction of loading, and with the 45°notch exactly centred. This ensured tha t the shear forces remained in plane, and eliminated unwanted bending force effects. There was no preloading of these specimens.

Shear load was applied to each specimen through the area of interest (the cross section between the vertices of the V-notches), at a constant displacement of 2.0mm/minute. The displacement was measured with a Mitutoyo® linear displacement gauge of resolution 0.01mm. The gauge was set up to measure parallel to the displacement of the apparatus.

The specimens were loaded until fracture occurred. Readings were taken throughout the test to use for the shear strength calculations. A representation, detailing the shear test setup, is shown below as ***Figure 14***.

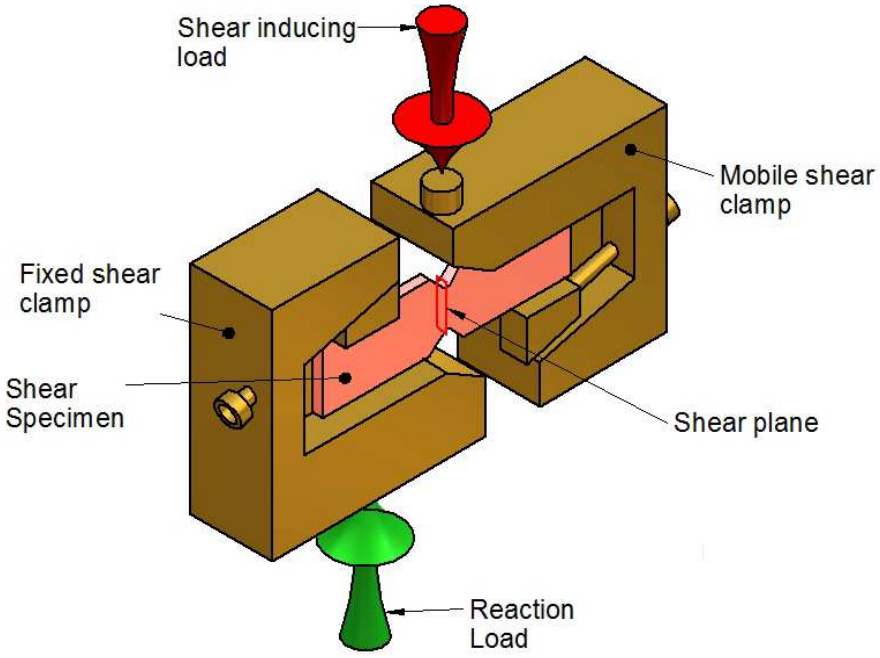


Figure 14: Shear strength test setup

3.4 STATISTICAL METHODS

The *Statistical Package for Social Sciences*® (SPSS), version 15.0 (SPSS Inc., Chicago, Illinois, USA) was used to analyse the data. The coefficient of variation (CV) indicated the relative magnitude of the standard deviation (SD), as compared with the mean of the distribution of measurements as a percentage (Leedy, 1985:195). The means of the five samples of each of the six treatment groups, as these related to each of the seven outcome measures *viz.* compressive strength$_{(max)}$ and modulus, flexural strength$_{(max)}$ and modulus, tensile strength$_{(max)}$ and modulus, and shear strength$_{(max)}$ were compared using one-way analysis of variance (ANOVA) testing.

Post-hoc Bonferroni-adjusted multiple comparison tests were done to assess which specific treatment groups differed significantly from each other. A p-value < 0.05 was considered to be statistically significant, at a 95% confidence interval. The statistical data was presented as tabulations of means, SDs and CVs, box-and whisker plots of median (50%) 25 percentile and 75 percentile distributions and ranges, and scatter plots as means of defining the mathematical relationship existing between individual data sets.

CHAPTER FOUR: THE RESULTS

4.1 INTRODUCTION

Post processed results for each test (as described in the previous chapter) are presented here. Where possible, data has been presented in a graphical manner for clarity and ease of interpretation.

4.2 EXOTHERMIC POLYMERISATION CYCLE TEST RESULTS

Table 5, below, depicts the mean (maximum) temperature (in ˚C), the standard deviation- (SD), and the coefficient of variance (CV) values for the six sample sets of the exothermic polymerisation test samples (Group E). As elaborated in the previous chapter, the samples for exothermic polymerisation testing, were designated in terms of their respective percentages of HA (*viz.* G0E, G5E, etc). The exothermic polymerisation cycle test results for all specimens of group E are summarised as *Appendix A*.

	G0E	G5E	G10E	G15E	G20E	G25E
Mean	120.8	111.0	109.4	107.4	106.4	102.8
SD	5.31	5.17	0.95	3.22	2.07	2.98
CV	0.07	0.07	0.01	0.05	0.04	0.04

Table 5: Mean temperature (in˚C), standard deviation (SD) and coefficient of variance (CV) values for the exothermic polymerisation cycle test

The reader's attention is drawn to an observed downward trend in the exothermic maximum mean as the HA percentage was increased. The nature of the decrease in exothermic maximum temperature as HA percentage increased is more clearly appreciated by reference to its graphic representation as ***Figure 15***, below

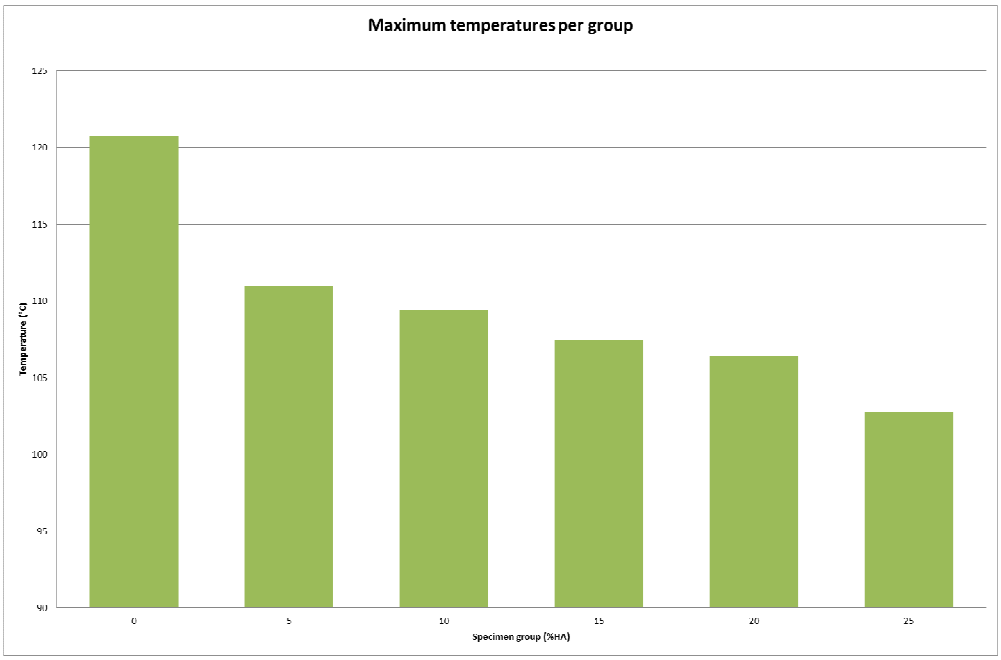


Figure 15: Mean (maximum) exothermic temperatures as a function of the percentage HA

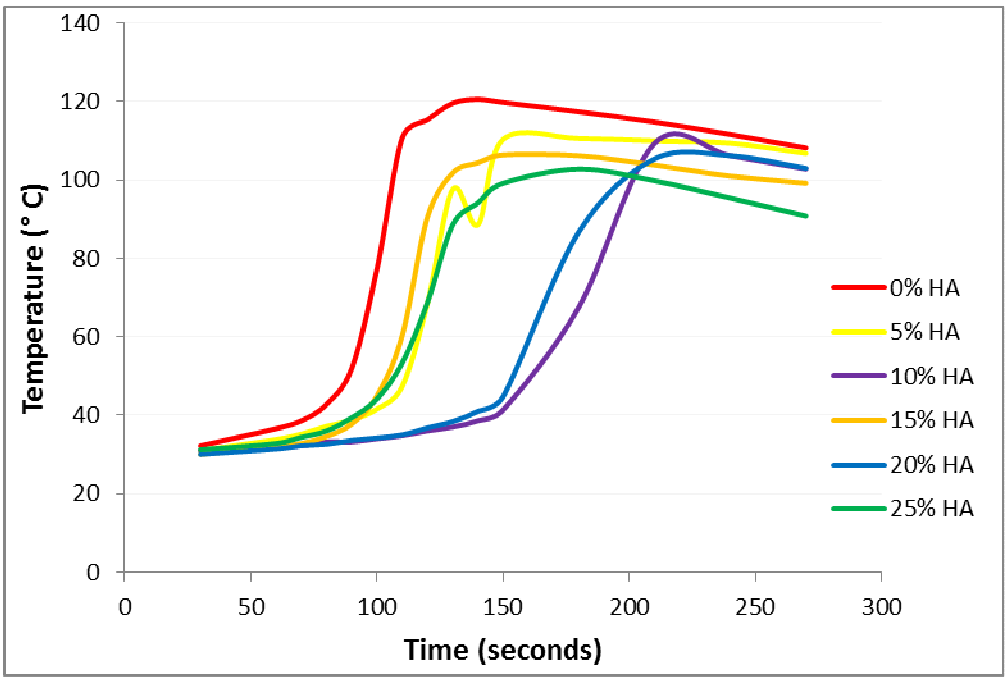


Figure 16: Temperature versus Time for each sample group

The changes in temperature, against time, for each sample group is shown in ***Figure 16***, above. In addition to recording the mean (maximum) exothermic

temperatures, as presented in ***Table 5***, above, it is also important, in terms of the objectives of the study, to chart the progress of temperature change through the process of curing (i.e. towards the achievement of the respective maximum exothermic temperature, and subsequent cooling).

4.3 MECHANICAL TEST RESULTS

In keeping with the previously described system of group designators, mechanical test samples were identified by the respective designators F (flexural), C (compressive), T (tensile) and S (shear).

4.3.1 FLEXURAL TEST RESULTS

4.3.1.1 Flexural Strength Results

Table 6, below, depicts the mean maximum flexural strength (in MPa), the standard deviation and coefficient of variance values of the flexural strength (Group F) sample groups. The flexural strength test results for all specimens of Group F are summarised as *Appendix B*.

	G0F	G5F	G10F	G15F	G20F	G25F
Mean	63.1067	52.6483	44.8927	37.1530	35.1879	31.4851
SD	6.66180	7.08169	8.80264	6.31687	3.34938	9.23895
CV	10.5	13.4	19.6	17.0	9.5	29.3

Table 6: Mean (in MPa), standard deviation and coefficient of variance values for flexural strength

Figure 17, below, further depicts the median (50th percentile), 25th and 75th percentiles (interquartile range) as well as the range of flexural strength values for Group F. It is noteworthy that the 25 percent HA composite displays both reduced values of flexural strength and an increasing tendency to unexpected fracture at the 75 percentile range. These observations, coupled with the trend

towards decreasing flexural strength as HA concentration increases towards the maximum of 25 percent, is consistent with HA's being recognized as a brittle material (Vallo *et al.*, 1999).

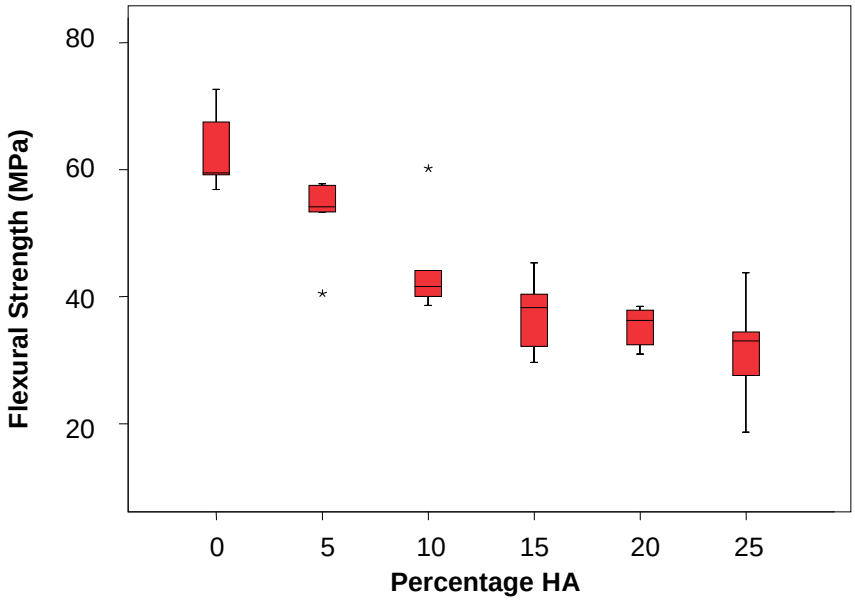


Figure 17: Box and whisker plot for flexural strength as HA percentage increases

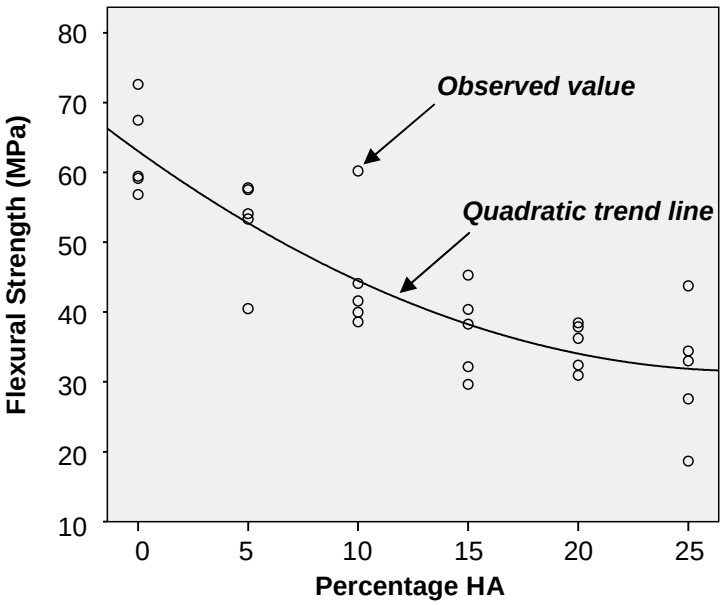


Figure 18: Scatter plot showing the quadratic relationship between HA percentage and maximum flexural strength

Figure 18, above, presents the relationship existing between increasing HA percentage and maximum flexural strength. A quadratic equation trend line correlates best with the measured results.

A comparison of *post-hoc* p-values for maximum flexural strength of the six sample groups, including the control group (G0F), is provided in ***Table 7***. Statistically significant p-values were found to exist between pure PMMA and all composites containing more than 10 percent HA, and between the 5 percent PMMA/HA composite and those composites containing more than 15 percent HA.

Inter-group Comparison		**p-value**
Group 1	***Group 2***	
G0F	G5F	0.451
	G10F	***0.008***
	G15F	***0.000***
	G20F	***0.000***
	G25F	***0.000***
G5F	G10F	1.000
	G15F	***0.032***
	G20F	***0.012***
	G25F	***0.001***
G10F	G15F	1.000
	G20F	0.641
	G25F	0.103
G15F	G20F	1.000
	G25F	1.000
G20F	G25F	1.000

Table 7: **Post-hoc *p-values for maximum flexural strength test***
(p < 0.05 indicates statistical significance)

4.3.1.2 Flexural Modulus Results

Table 8 depicts the mean flexural modulus values for the six flexural strength test groups (group F). The flexural modulus for each specimen was calculated according to its formula before the statistical mean flexural modulus (in GPa),

standard deviation and coefficient of variance values were determined. The flexural modulus values are summarised as Appendix B(i) – B(vi).

	G0F	G5F	G10F	G15F	G20F	G25F
Mean	2.9496	2.7709	2.8840	2.8814	3.4084	3.1327
SD	0.64607	0.17217	0.35789	0.46267	0.24603	0.51076
CV	21.9	6.2	12.4	16.0	7.2	16.3

Table 8: Mean (in GPa), standard deviation and coefficient of variance values for flexural modulus

Figure 19 depicts the median (50th percentile), 25th and 75th percentiles (interquartile range) as well as the range of flexural modulus values for Group F.

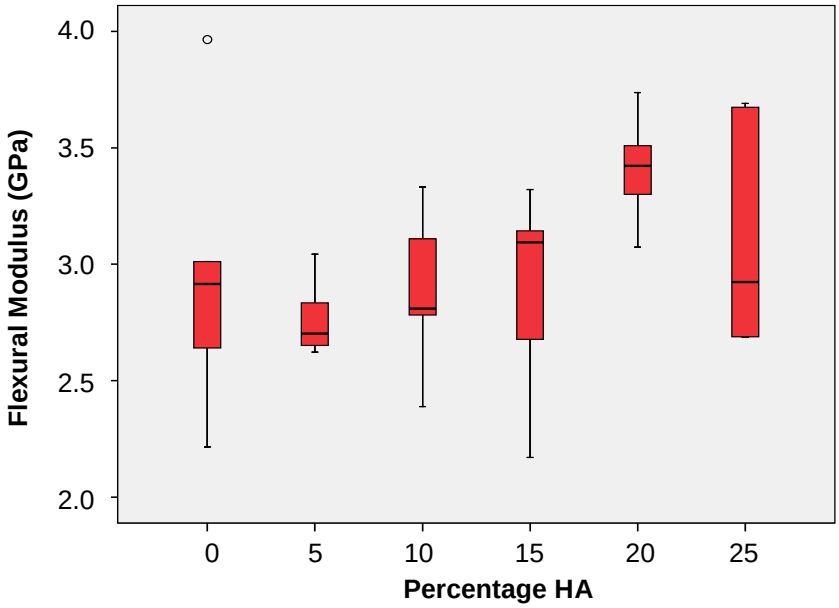


Figure 19: Box and whisker plot for flexural modulus as HA percentage increases

A comparison of *post-hoc* p-values for flexural modulus of the five composite sample groups against the pure PMMA control group, and each other, is presented in ***Table 9***. There are no statistically significant differences in flexural modulus between the six groups.

Inter-group Comparison		p-value
Group 1	*Group 2*	
G0F	G5F	1.000
	G10F	1.000
	G15F	1.000
	G20F	1.000
	G25F	1.000
G5F	G10F	1.000
	G15F	1.000
	G20F	0.416
	G25F	1.000
G10F	G15F	1.000
	G20F	0.988
	G25F	1.000
G15F	G20F	0.969
	G25F	1.000
G20F	G25F	1.000

Table 9:* Post-hoc *p-values for flexural modulus

4.3.2 COMPRESSIVE TEST RESULTS

4.3.2.1 Compressive Strength Results

Table 10, below, depicts the mean maximum compressive strength (in MPa), the standard deviation, and the coefficient of variance for each of the six compressive strength (Group C) sample groups. The compressive strength results for all specimens of Group C are summarised as *Appendix C*.

	G0C	G5C	G10C	G15C	G20C	G25C
Mean	82.4860	78.1100	75.3840	74.6480	71.9140	68.700
SD	0.84435	6.84634	1.14531	1.74186	4.49665	7.64371
CV	0.01	0.08	0.01	0.02	0.06	0.11

Table 10: Mean (in MPa), standard deviation and coefficient of variance values for compressive strength

Figure 20, below, depicts the median, 25th and 75th percentiles as well as the

range of compressive strength values for the Group C samples. A trend towards a decrease in compressive strength as HA percentage is increased is observed.

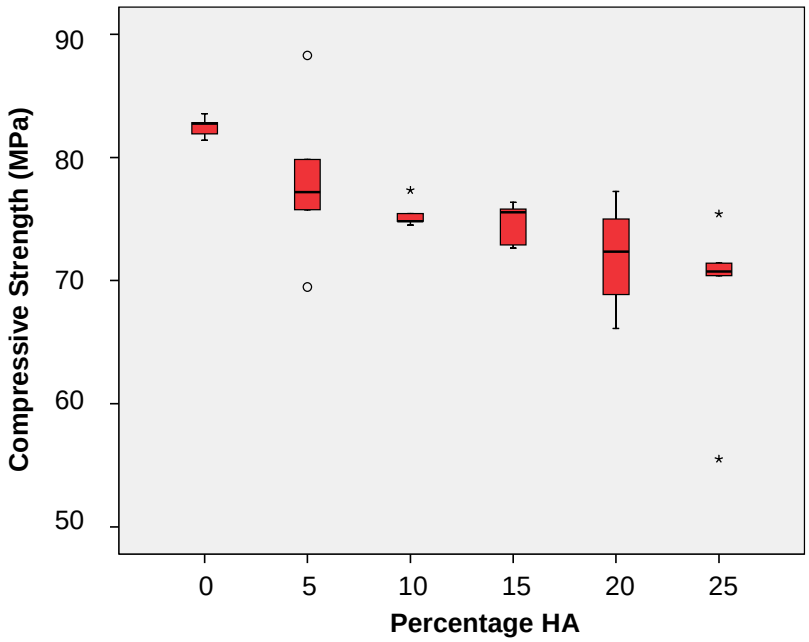


Figure 20: Box and whisker plot for compressive strength as HA percentage increases

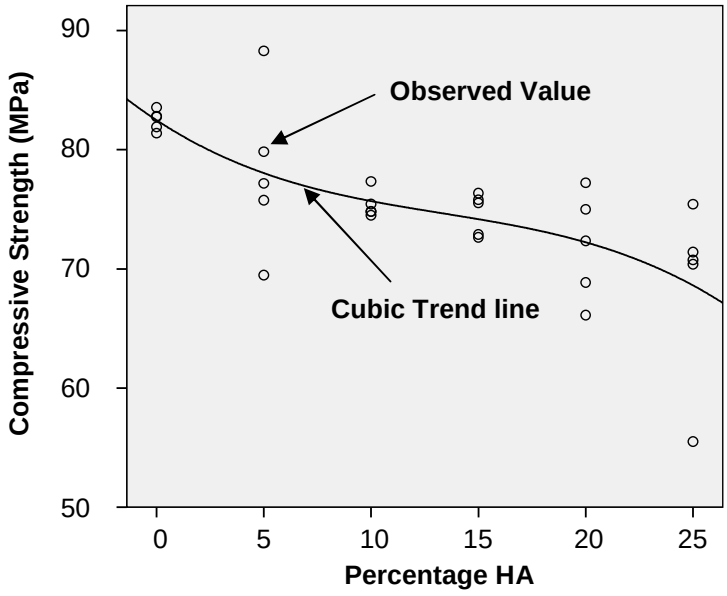


Figure 21: Scatter plot showing the cubic relationship between HA percentage and maximum compressive strength

Figure 21, above, similarly represents the relationship between increasing HA percentage and maximum compressive strength. In this scatter plot, the relationship is able to be represented by a cubic trend line that approximates the same curve.

A comparison of *post-hoc* p-values for maximum compressive strength of the five composite sample groups against the pure PMMA control group, and each other, is presented in ***Table 11***. There is a statistically significant difference only between pure PMMA (G0C) and the 25 percent HA group (G25C).

Inter-group Comparison		
Group 1	***Group 2***	**p-value**
G0C	G5C	1.000
	G10C	0.362
	G15C	0.207
	G20C	0.022
	G25C	***0.001***
G5C	G10C	1.000
	G15C	1.000
	G20C	0.696
	G25C	0.059
G10C	G15C	1.000
	G20C	1.000
	G25C	0.492
G15C	G20C	1.000
	G25F	0.827
G20C	G25F	1.000

Table 11: **Post-hoc *p-values for the maximum compressive strength test***

4.3.2.2 Compressive Modulus Results

In ***Table 12***, below, the mean compressive modulus values (including SD and CV) for the five PMMA/HA groups against pure PPMA, and against each other (Group C), are presented. The compressive modulus for each specimen was calculated using the formula presented in the *Definition of Terms,* before statistical analysis. The compressive modulus results for the individual

specimens of Group C are summarised as Appendix C(i) to C(vi).

	G0C	G5C	G10C	G15C	G20C	G25C
Mean	2.7713	2.2874	1.8007	2.7972	2.7100	2.8884
SD	0.64194	0.66286	0.95071	0.96271	0. 64914	0.57134
CV	0.23	0.28	0.52	0.34	0.23	0.19

Table 12: Mean (in GPa), standard deviation and coefficient of variance values for compressive modulus

Figure 22 depicts the median, 25th and 75th percentiles as well as the range of compressive modulus values for Group C. As was observed in ***Figure 19*** *[flexural modulus to HA percentage]*, above, there is no clear trend with reference to compressive modulus as HA percentage is increased.

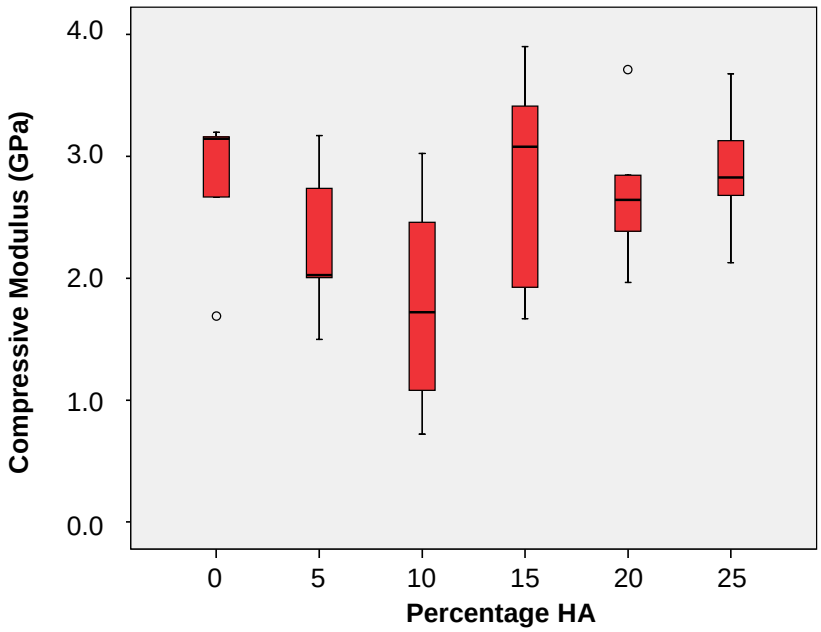


Figure 22: Box and whisker plot for compressive modulus as HA percentage increases

The comparison of *post-hoc* p-values for compressive modulus of the five sample groups against the control group, and between each other, is reflected below, as ***Table 13***. As was observed with reference to flexural modulus *[See Table 9, above]*, there were no statistically significant differences between the

six sample groups.

Inter-group Comparison		p-value
Group 1	***Group 2***	
G0C	G5C	1.000
	G10C	0.804
	G15C	1.000
	G20C	1.000
	G25C	1.000
G5C	G10C	1.000
	G15C	1.000
	G20C	1.000
	G25C	1.000
G10C	G15C	0.720
	G20C	1.000
	G25C	0.482
G15C	G20C	1.000
	G25C	1.000
G20C	G25C	1.000

Table 13:* Post-hoc *p-values for compressive modulus

4.3.3 TENSILE TEST RESULTS

4.3.3.1 Tensile Strength Results

As in previous tests, ***Table 14***, below, depicts the mean maximum tensile strength (in MPa), standard deviation, and coefficient of variance values of the six sample sets constituting Group T. The tensile strength test results for each individual specimen from Group T are summarised in *Appendix D*.

	G0T	G5T	G10T	G15T	G20T	G25T
Mean	29.5239	30.0500	30.5415	26.2695	20.0042	18.0234
SD	6.38266	3.43984	2.11482	2.53366	5.21477	3.68559
CV	21.6	11.4	6.92	9.64	26.0	20.4

Table 14: Mean (in MPa), standard deviation and coefficient of variance values for tensile strength

Figure 23 depicts the median, 25th and 75th percentiles as well as the range of tensile strength values for Group T.

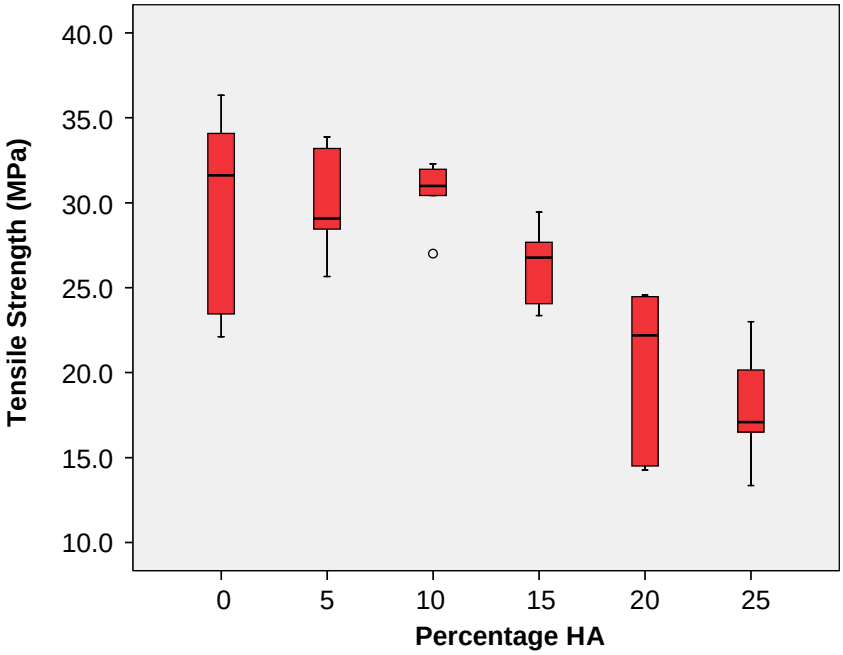


Figure 23: Box and whisker plot for tensile strength as HA percentage increases

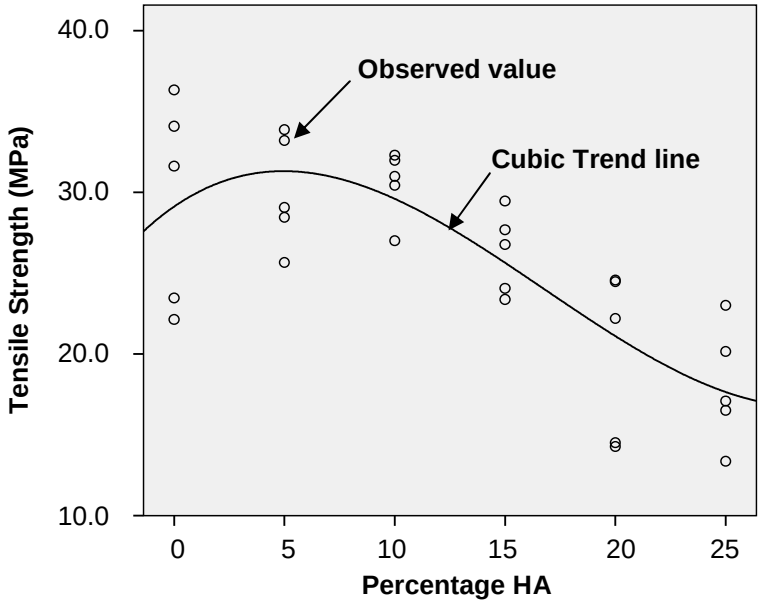


Figure 24: Scatter plot showing the cubic relationship between HA percentage and maximum tensile strength

Figure 24, above, represents the relationship between increased HA percentage and maximum tensile strength. As was observed previously, with reference to maximum compressive strength *[See Figure 21]*, the relationship of increased HA percentage to maximum tensile strength is best represented by a cubic trend line.

A comparison of *post-hoc* p-values for maximum tensile strength of the five composite sample groups against the pure PMMA control group, and each other, is presented in ***Table 15***. There are statistically significant differences between those samples containing less than ten percent HA (*viz.* G0T, G5T and G10T) and those containing at least 20 percent HA (*viz.* G20T and G25T).

Inter-group Comparison		
Group 1	***Group 2***	**p-value**
G0T	G5T	1.000
	G10T	1.000
	G15T	1.000
	G20T	***0.021***
	G25T	***0.003***
G5T	G10T	1.000
	G15T	1.000
	G20T	***0.013***
	G25T	***0.002***
G10T	G15T	1.000
	G20T	***0.008***
	G25T	***0.001***
G15T	G20T	0.387
	G25T	0.069
G20T	G25T	1.000

Table 15:* Post-hoc *p-values for maximum tensile strength test

4.3.3.2 Tensile Modulus Results

As previously, ***Table 16***, below, provides the descriptive statistics relating to the calculated tensile modulus (including mean, SD and CV) of the six sample sets

constituting Group T. The tensile strength test calculations for each individual specimen from Group T are summarised in Appendix D(i) – D(vi).

	G0T	G5T	G10T	G15T	G20T	G25T
Mean	2.6821	2.7274	2.7528	3.0076	2.7931	2.9057
SD	0.15440	0.07210	0.14685	0.08934	0.06379	0.09563
CV	5.75	2.64	5.33	2.97	2.28	3.29

Table 16: Mean (in GPa), standard deviation and coefficient of variance values for the tensile modulus

A comparison of *post-hoc* p-values for the tensile modulus of the five composite sample groups against the control group (G0T), and each other, are presented in ***Table 17***, below.

Inter-group Comparison		**p-value**
Group 1	***Group 2***	
G0T	G5T	1.000
	G10T	1.000
	G15T	***0.001***
	G20T	1.000
	G25T	0.053
G5T	G10T	1.000
	G15T	***0.007***
	G20T	1.000
	G25T	0.248
G10T	G15T	***0.018***
	G20T	1.000
	G25T	0.554
G15T	G20T	0.073
	G25T	1.000
G20T	G25T	1.000

Table 17:* Post-hoc *p-values for tensile modulus

The data suggest that there is a statistically significant difference between those composites containing between zero (i.e. pure PMMA) to ten percent HA, and a composite containing 15 percent HA. Increasing the HA content beyond 15

percent, however, does not produce a similar effect, since a statistically significant difference is not observed between the low HA percentage composites (i.e. zero, five and ten percent HA samples) and the 20 percent and 25 percent samples, nor between the 15 percent composite and the higher percentage HA samples.

Figure 25, below, which depicts the median, 25th and 75th percentiles as well as the range of tensile modulus values for Group T, similarly shows that the 15 percent HA sample demonstrated tensile modulus values that were extraordinarily higher than an otherwise linear trend may have suggested.

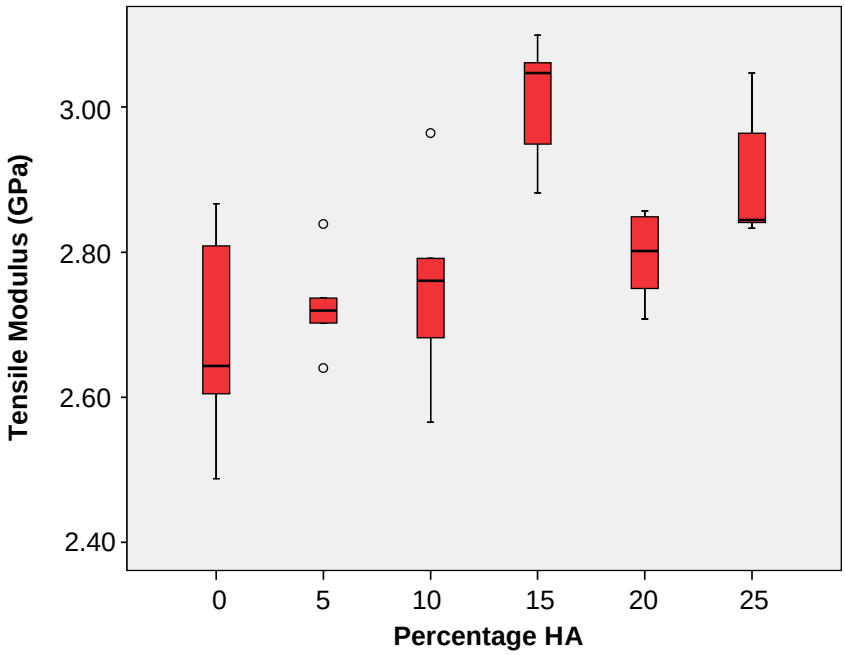


Figure 25: Box and whisker plot for tensile modulus as HA percentage increases

4.3.4 SHEAR STRENGTH TEST RESULTS

Table 18 depicts the mean maximum shear strength value (in MPa), standard deviation, and coefficient of variance values of the six sample sets comprising Group S. The shear strength test results for each specimen of group S, as

previously, are summarised as *Appendix E*.

	G0S	G5S	G10S	G15S	G20S	G25S
Mean	23.6264	19.1907	16.9208	14.3319	9.1750	9.7225
SD	1.92089	1.50313	0.59945	4.19473	5.40129	4.20747
CV	8.13	7.83	3.54	29.2	58.8	43.2

Table 18: Mean (in MPa), standard deviation and coefficient of variance values for shear strength

Figure 26 depicts the median, 25th and 75th percentiles as well as the range of shear strength values for Group S.

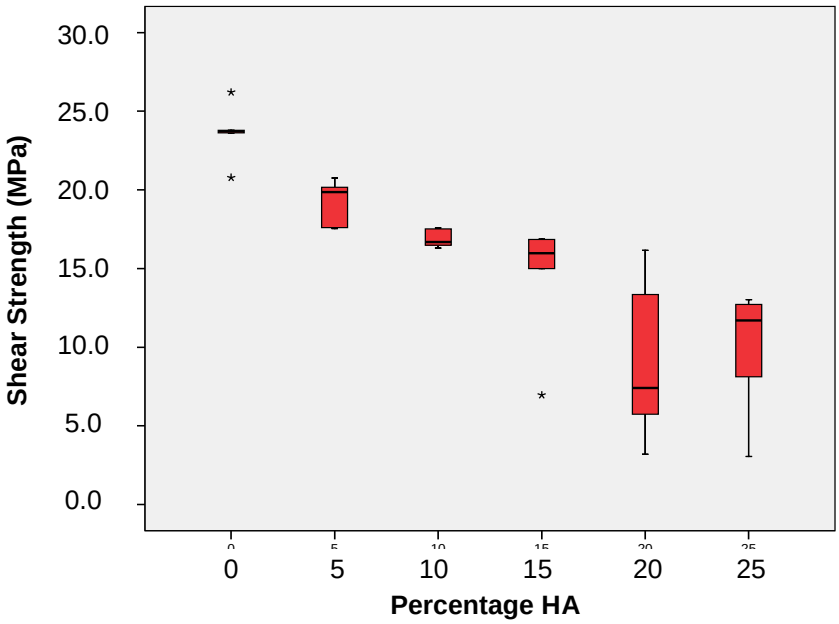


Figure 26: Box and whisker plot for shear strength as HA percentage increases

Figure 27, below, represents the relationship between maximum shear strength and increasing percentages of HA within PMMA/HA composites. This relationship may be best-represented by a linear trend line, which would, therefore, suggest a simple and direct relationship in which any increase in the percentage HA within a PMMA/HA composite would result in a commensurate decrease in the shear strength of the composite.

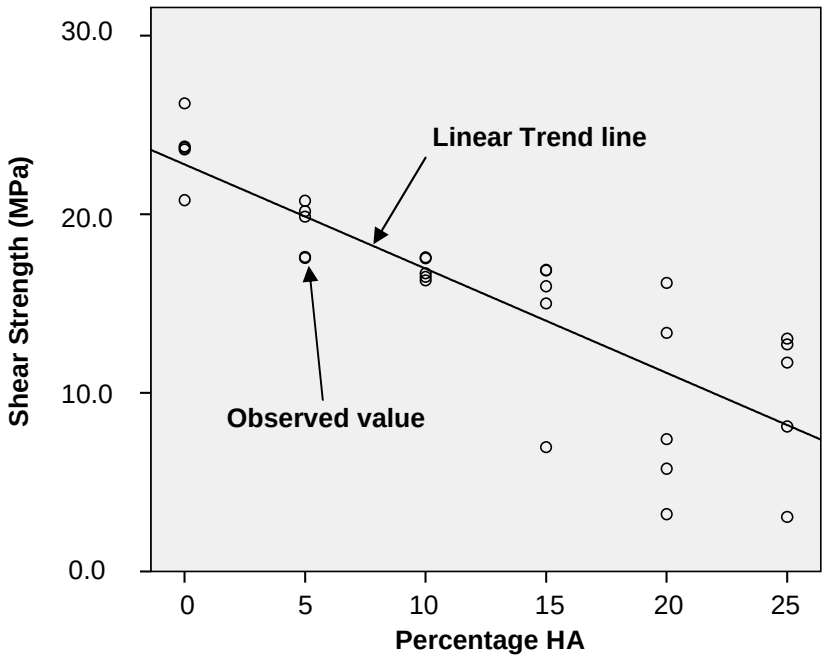


Figure 27: Scatter plot showing the linear relationship between HA percentage and maximum tensile strength

Inter-group Comparison		p-value
Group 1	***Group 2***	
G0S	G5S	0.784
	G10S	0.076
	G15S	***0.004***
	G20S	***0.000***
	G25S	***0.000***
G5S	G10S	1.000
	G15S	0.523
	G20S	***0.002***
	G25S	***0.003***
G10S	G15S	1.000
	G20S	***0.023***
	G25S	***0.044***
G15S	G20S	0.389
	G25S	0.665
G20S	G25S	1.000

Table 19:* Post-hoc *p-values for the maximum shear strength test

A comparison of *post-hoc* p-values for maximum shear strength of the five

PMMA/HA sample groups against the PMMA control (G0S), and against each other suggests a statistically significant reduction in shear strength, relative to pure PMMA, in all composites containing 15 or more percent HA. The data, further, suggest that composites containing 20 or 25 percent HA display significantly less shear strength than those containing either five or ten percent HA. There is no statistically significant loss of shear strength in the 15 to 25 percent HA range.

CHAPTER FIVE: THE DISCUSSION

5.1 INTRODUCTION

An interpretation and discussion of the results presented in previous chapter is offered in this chapter. Where relevant, the relationship of the interpreted results to the characterisation of the respective PMMA/HA composites in terms of their thermal curing- and mechanical properties is also included.

5.2 EXOTHERMIC POLYMERISATION CYCLE TEST RESULTS

The decrease of the exothermic reaction arising from polymerisation during the rendering of an *in situ* prosthetic would be advantageous, since a recipient of the resultant prosthesis would not need to withstand excessively high temperatures where small repairs are to be made. More extensive repairs with a reduction of associated tissue damage would be able to be made, *in situ*, if the exothermic reaction were to yield a temperature spectrum that was sufficiently low. Increasing the HA percentage has been observed to enhance the characteristics of the composite material, not only as a bioactivity enhancer (increasing the adherence to bone) but also, though to a lesser extent, the working and cured properties. Hydroxyapatite, as a filler-reinforcement, is able to both reduce the shrinkage of the resultant composite and, evidently, decrease the mean maximum temperature arising from the polymerisation process. Since high temperatures are known to cause tissue necrosis, the latter advantage assumes some relevance, especially since self-cure materials are often utilised *in vivo* with direct bone contact occurring during the cure cycle.

In ***Figure 28***, below, it can be seen that the mean maximum temperature values decrease with increasing HA content. The mean (maximum) exothermic temperatures of all six groups were, however, above 100˚C, with small relative

temperature reductions as the HA percentage increased. The largest single reduction (of 9.8˚C) occurred between zero percent and five percent HA. The maximum temperature reduction of 18˚C, between a composite of 25 percent HA and pure PMMA, a reduction of the mean maximum temperature from 120.8 ˚C to 102.8˚C), may not, in practice be sufficient, however, to allow for application of such a composite in extensive repairs where the resultant tissue damage would carry greater clinical impact. The CV values for all of the test groups were less than 0.1, indicating high repeatability in the measures and that the effect may be regarded as reliable.

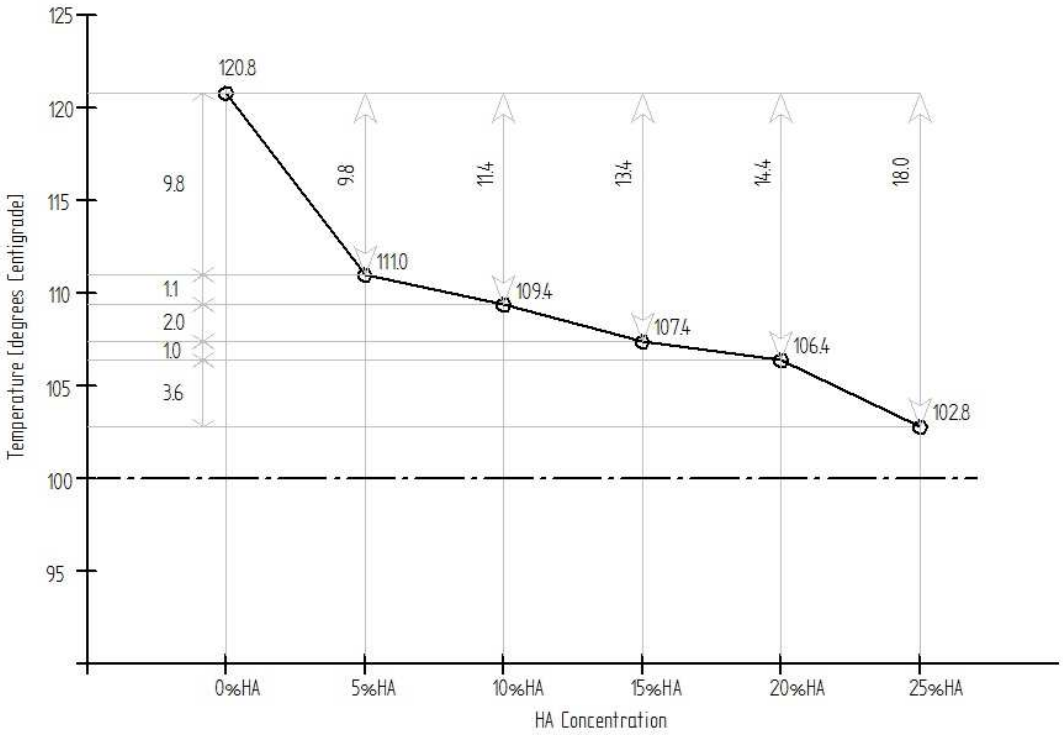


Figure 28: Relationship of the maximum temperature values to increased HA concentration

In ***Figure 16*** *[See Section 4.2 above]*, it was demonstrated that the addition of HA also delays the onset of the exothermic maximum temperature, indicating a delay in polymerisation initiation. This may be tested in a future study to determine the extent to which this delay translates into a longer working time, a possible advantage, in a clinical context, to the respective health professional.

5.3 FLEXURAL TEST RESULTS

5.3.1 FLEXURAL STRENGTH RESULTS

When a length of beam is acted upon by a constant bending moment (zero shear force) then the stresses set up on any cross section must constitute a pure couple equal in magnitude to the initial bending moment. The maximum stress capability when loaded in this manner is the maximum flexural strength. (Ryde.,1974). Bending loads are extremely common in a variety of applications, and it is likely to be in evidence in a range of, particularly cranial, prosthetics when a load (distributed or point) is to be applied anywhere within the extent of the prosthesis. The reaction to this load would be distributed along the area where the prosthesis is attached to natural bone, thereby setting up a bending (or flexing) scenario. Flexural strength is the maximum load (in bending) that the material can withstand before failure.

In ***Figure 29***, below, it may be observed that flexural strength decreases with increasing HA percentage. The SD results, as reflected in ***Table 6*** *[See Section 4.3.1.1]* indicated acceptable testing accuracy at the 95% CI for the flexural strength tests conducted in this study. The CV value of the 25 percent HA samples, at 29.3 is higher than the previous five groups containing less HA, suggesting that the material reproducibility, and reliability, may decline when such relatively high concentrations of HA are included within the composites. This has previously been described as attributable to the recognised brittleness of HA itself (Vallo *et al.*, 1999).

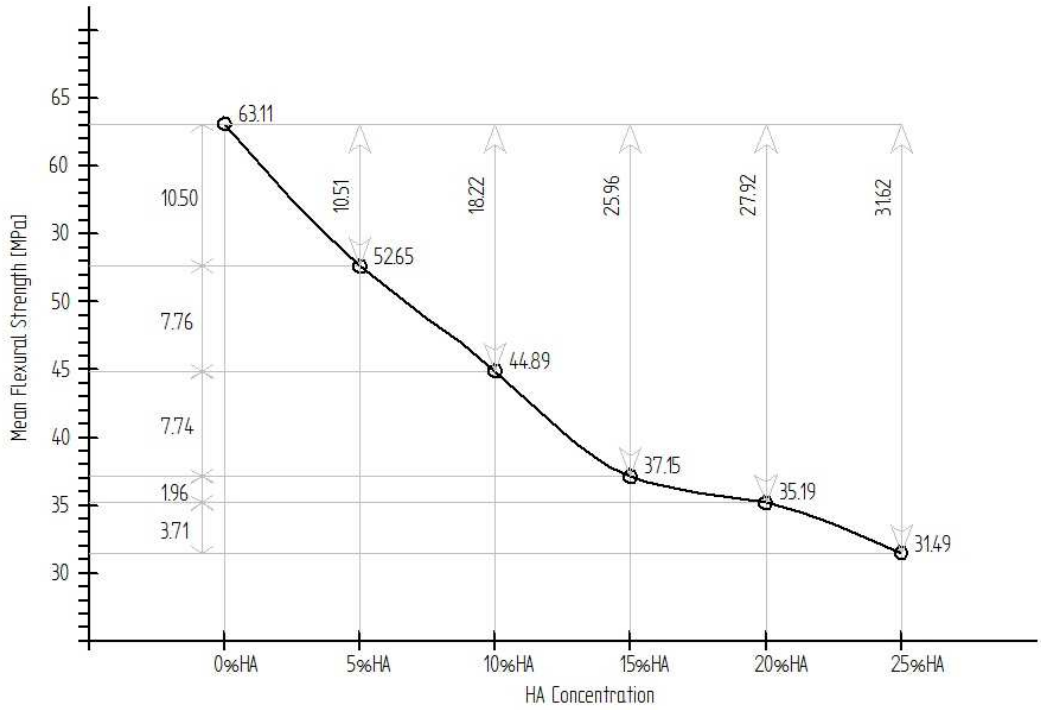


Figure 29: Relationship of mean flexural strength to increased HA concentration

Closer inspection of the described reduction of flexural strength as HA concentration is increased reveals that the most notable reduction of flexural strength occurs below the 15 percent HA level, with the reduction appearing to level off above the 15 percent threshold. Between the pure PMMA group (63.1 MPa) and the 25 percent HA group (31.5 MPa) a total reduction of 31.6 MPa of flexural strength was observed, representing a 50 percent decrease in flexural strength across the range. The reduction in flexural strength, between pure PMMA and 15 percent HA is calculated to be 41.13 percent with a further reduction of 8.87 occurring between 15 and 25 percent HA.

The evident reduction of flexural strength with relatively low percentages of HA is further demonstrated in ***Table 20***, below, in which it may be observed that the addition of any percentage of HA above ten percent resulted in a significant reduction in flexural strength, relative to pure PMMA, but that there was no statistically significant further reduction of flexural strength between this

threshold level and the 25 percent maximum.

	0%	5%	10%	15%	20%	25%
0%						
5%	0.451					
10%	***0.008***	1.000				
15%	***0.006***	***0.034***	1.000			
20%	***0.000***	***0.012***	0.641	1.000		
25%	***0.000***	***0.001***	0.163	1.000	1.000	

Table 20: Summarised comparative p-values for flexural strength

The trend further suggest that increasing the HA concentration to 25 percent, or beyond, may result in unpredictable flexural strength. This was seen in the dramatically increased lower 75th percentile values for the 25 percent HA group. When consideration is made that an greater specimen number may indeed increase (but not decrease) the lower 75th percentile range, the increased likelihood of potential failure in 25 percent HA composites ought not to be underestimated.

The strength requirements of prosthetic materials depend on the size, design and function of the resultant prosthesis. Of some concern, in this regard, would be the evident reduction in flexural strength as compared to the pure PMMA control group, (a proven repair material), by the addition of HA, since even relatively small additions of HA significantly reduce this parameter of strength.

This would be need to be offset, clinically, by the advantages of including HA, in terms of improved bioactive bonding, which would facilitate reliable maintenance of the position of the prosthetic (Serbetci *et al.*, 2003), and the reduced shrink on curing. In this regard, it would appear reasonable to recommend that the minimum percentage of HA to gain sufficient bioactive bonding capacity be considered, as higher percentages do represent an inevitable further loss of flexural strength. The results of this study, further, would appear to support the view in the literature that 15 percent HA represents the best compromise of bioactivity and strength (Moursi *et al.*, 2001).

5.3.2 FLEXURAL MODULUS RESULTS

Flexural modulus is the ratio of the bending stress to bending strain within the elastic limits of the material (Juvinall *et al.*, 1991). This is an indication of the material's ability to withstand bending deflection when a load is applied. In the case of a prosthesis, this would be coupled with a second moment, that of area, to determine the ability of the prosthesis to resist bending.

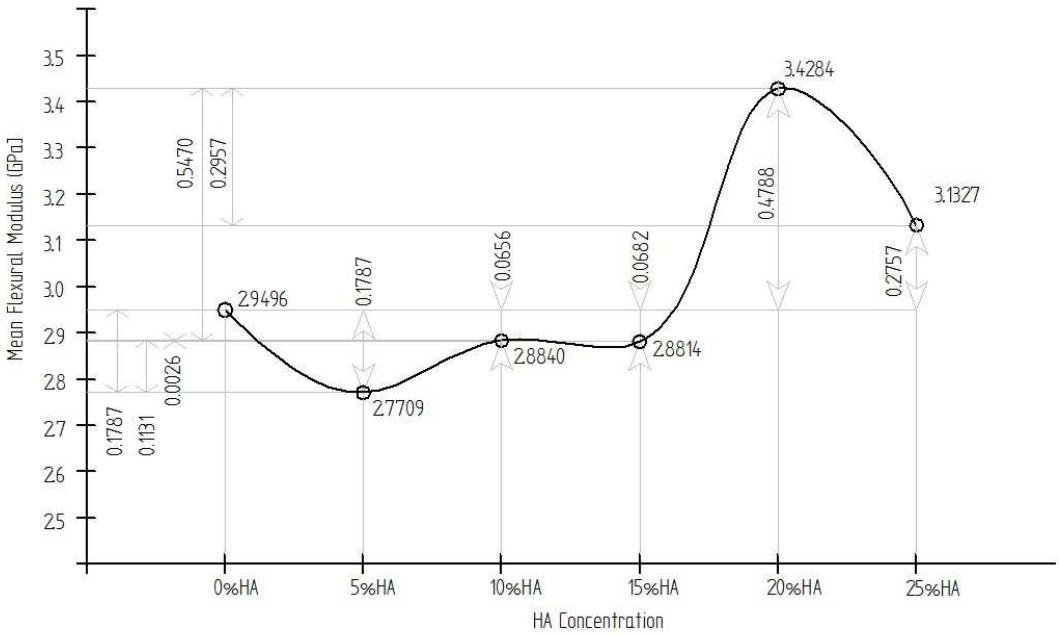


Figure 30: Relationship of mean flexural modulus to increased HA concentration

In ***Figure 30***, above, it can be observed that that the mean value of the flexural modulus fluctuated in a gently positive direction as the HA percentage increased, but no clear correlations were able to be noted. This is supported, further, in ***Table 21***, below, in which it is clear that no statistically significant effect on flexural modulus is created by the addition of HA. The gentle upward trend does, however, suggest that a resultant prosthesis would show a subtly increased rigidity with increasing concentrations of HA.

	0%	5%	10%	15%	20%	25%
0%						
5%	0.451					
10%	1.000	1.000				
15%	1.000	1.000	1.000			
20%	1.000	0.416	0.988	0.969		
25%	1.000	1.000	1.000	1.000	1.000	

Table 21: Summarised comparative p-values for flexural modulus

5.4 COMPRESSIVE TEST RESULTS

5.4.1 COMPRESSIVE STRENGTH RESULTS

Compressive strength refers to the stress a material can withstand when the load creating that stress is applied axially and the forces act toward each other,

through the material in question (Juvinall *et al.*, 1991). In the case of maxillo-facial prosthetics, for instance, this may occur through loads resulting in skull compaction or crushing.

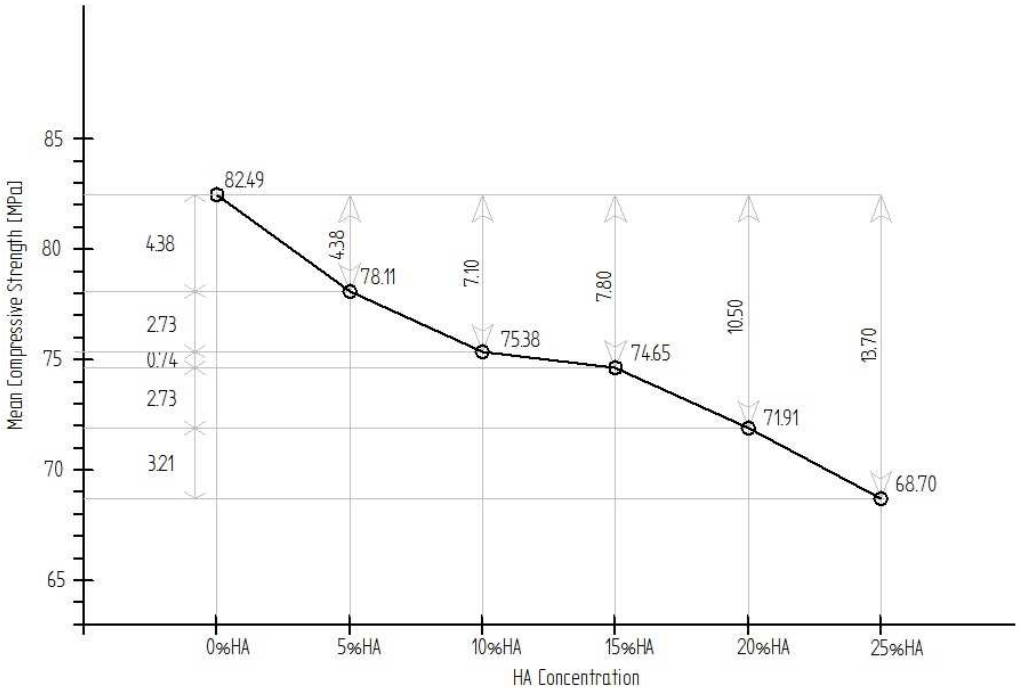
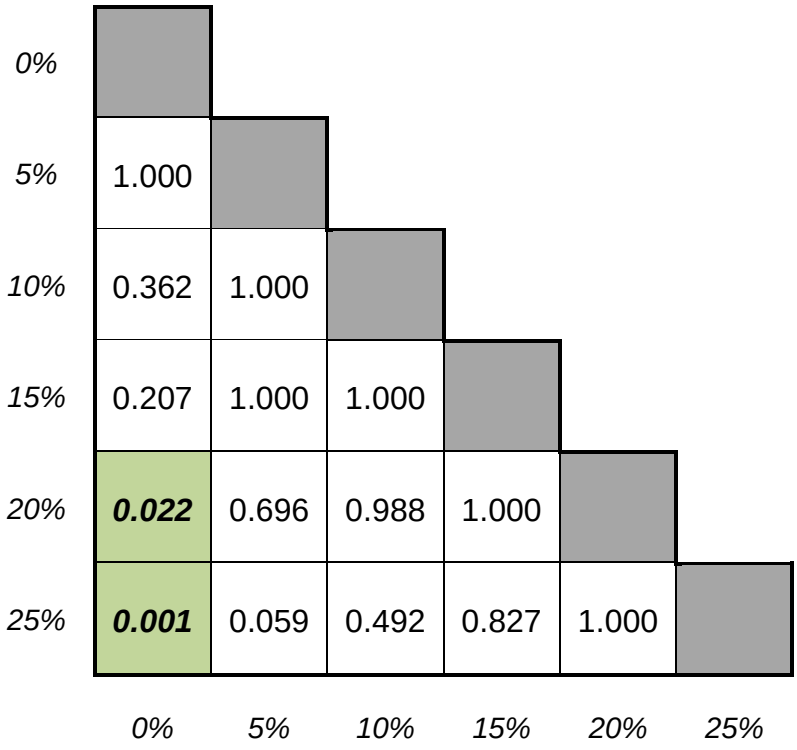


Figure 31: Relationship of mean compressive strength to increased HA concentration

In ***Figure 31***, above, it can be seen that the compressive strength decreases with increasing HA percentage.

Consideration of the CV values contained in ***Table 10*** *[See Section 4.3.2.1]*, reveals that most values are very low *[ranging between 0.01 and 0.11]*. This would suggest a consistent compressive strength performance of the PMMA/HA composite, across the range of HA percentages. Notwithstanding, it ought to be noticed, too, that the 25 percent HA samples produced both a relatively higher SD *[7.64371]* and higher CV *[0.11]* than all other sample sets. Only the five percent HA *[SD: 6.84634; CV: 0.06]* and 20 percent HA *[SD: 4.49665; CV: 0.08]* sample sets, displayed comparable, if not as notably high SD and CV values.



	0%	5%	10%	15%	20%	25%
0%						
5%	1.000					
10%	0.362	1.000				
15%	0.207	1.000	1.000			
20%	***0.022***	0.696	0.988	1.000		
25%	***0.001***	0.059	0.492	0.827	1.000	

Table 22: Summarised comparative p-values for compressive strength

The suggestion that HA concentrations of HA above 20 percent are relatively less stable with respect to compressive strength performance, is further supported by the observation, in ***Table 22***, above, that the 20 and 25 percent HA specimens are statistically significantly different, in terms of compressive strength performance, to pure PMMA, although the p-values do not suggest that, in themselves, these concentrations are statistically different to composites containing lower percentages of HA (*viz.* five-, ten- and 15 percent HA)

In ***Figure 21*** *[See Section 4.3.2.1]* attention was drawn to the approximated cubic relationship that exists between compressive strength and HA percentage. This apparent mathematic relationship would allow for accurate estimation of compressive strength values against respective specific HA percentages within the zero to 25 percent HA range. The data, as stated, indicates that compressive strength differences become significant at the 20 percent HA threshold, although this may ultimately be found to be at a lower intermediary

point between the 15- and 20 percent HA concentrations.

5.4.2 COMPRESSIVE MODULUS RESULTS

The compressive modulus describes the ratio of strain to an applied stress for a specific material, and may be interpreted as a measure of the resistance of the material to dimensional change for a corresponding compressive load (Ryder, 1974). The significance of this to prosthetic application is that it would indicate the ability of the material to keep its shape under loading conditions (coupled with the second moment, that of area, which is a function of the specific prosthesis geometry).

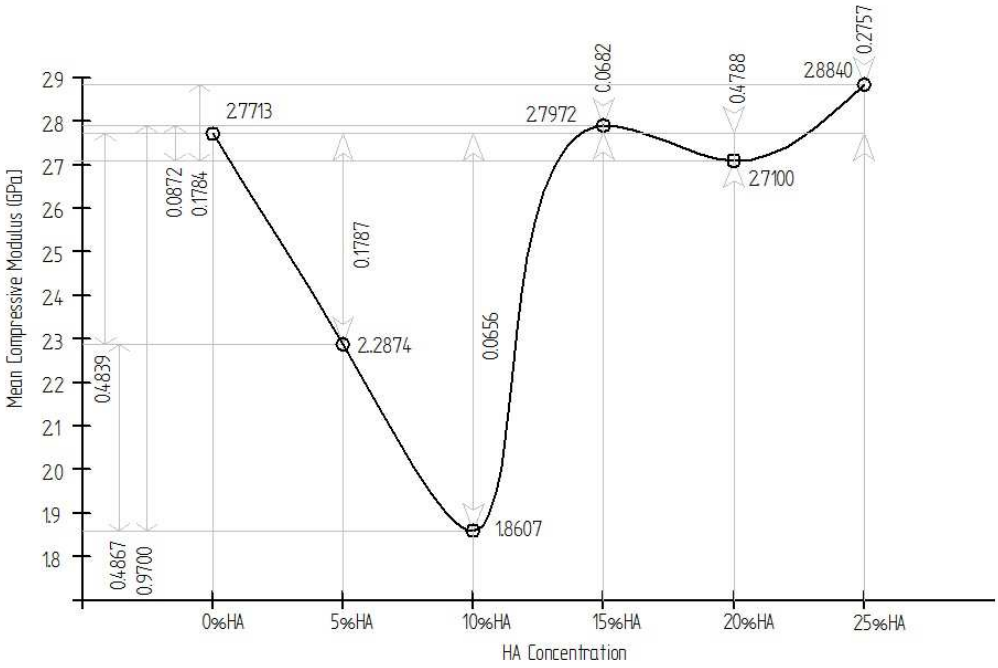


Figure 32: Relationship of mean compressive modulus to increased HA concentration

Figure 32, above, in combination with the summarized comparative p-values reflected in ***Table 23***, below, suggests that there are no significant differences in compressive modulus through the range of HA composite samples. It is worthwhile, however, to note that, although not statistically significant, the lower

concentrations of HA (i.e. 5 percent and 10 percent) appear to have an effect on compressive modulus which is outside of the relatively narrow range of the other samples *[2.7100 – 2.8840 GPa]*.

	0%	5%	10%	15%	20%	25%
0%						
5%	1.000					
10%	0.804	1.000				
15%	1.000	1.000	0.720			
20%	1.000	1.000	1.000	1.000		
25%	1.000	1.000	0.482	1.000	1.000	

Table 23: Summarised comparative p-values for compressive modulus

5.5 TENSILE TEST RESULTS

5.5.1 TENSILE STRENGTH RESULTS

Tensile strength is the maximum stress that a material can withstand when the loads causing that stress are applied axially, and act so as to separate the material in question (Juvinall *et al.*, 1991). In the case of prosthetics, tensile loads would be those applied to one side of an object subjected to a bending load. Such forces would be encountered within, *inter alia*, the maxillofacial context.

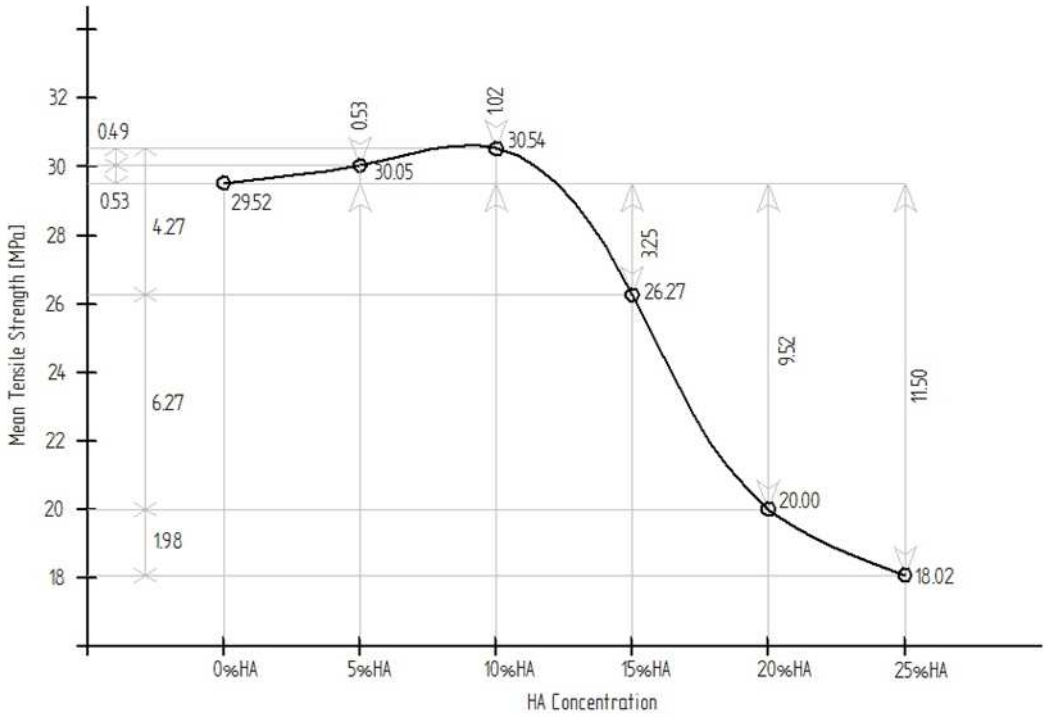


Figure 33: Relationship of mean tensile strength to increased HA concentration

In ***Figure 33***, above, it may be observed that tensile strength is non-significantly increased by the addition of low concentrations of HA, peaking at 30.5MPa at the 10 percent HA concentration. At higher concentrations, tensile strength is adversely affected by the further addition of HA, and this assumes statistical significance at the 20 percent- *[p = 0.08 – 0.21]* and 25 percent HA *[p = 0.01 – 0.03]* concentrations (see ***Table 24*** ,below).

In ***Figure 21*** *[See Section 4.3.3.1]* it was shown that the mathematical relationship of HA concentration to tensile strength followed a cubic distribution. In terms of the interpolated cubic curve, it may be calculated that the peak tensile strength (of around 32MPa) may be expected at a concentration of five percent HA, with a non-significant reduction as the HA percentage is increased towards the 20 percent concentration.

	0%	5%	10%	15%	20%	25%
0%						
5%	1.000					
10%	1.000	1.000				
15%	1.000	1.000	1.000			
20%	***0.021***	***0.013***	***0.008***	0.387		
25%	***0.003***	***0.002***	***0.001***	0.067	1.000	

Table 24: Summarised comparative p-values for tensile strength

The statistical analysis, in terms of p-values, would suggest that the addition of HA to a composite up to a concentration of 15 percent, does not significantly decrease the resultant tensile strength relative to pure PMMA. The significant loss of tensile strength at higher concentrations, however, suggests that the maximal concentration of HA, in terms of its desirable bioactive properties, would need to approximate the 15 percent level.

5.5.2 TENSILE MODULUS RESULTS

Tensile modulus, or Young's modulus, is a measure of the ratio of material stress to strain in elastic tensile loading conditions (Ryder, 1974). Put more simply, it is the resistance of the material to geometrical change for a given tensile load. The tensile modulus is therefore an important measure of the stiffness of the prosthetic material and is required when designing the prosthesis to ensure that any deflection under the known tensile loading

conditions is within acceptable limits.

Figure 34, below, indicates that the mean value of the tensile modulus increased as the HA percentage increased, with a maximal mean tensile modulus achieved at the 15 percent HA concentration *[3.0076 GPa]*.

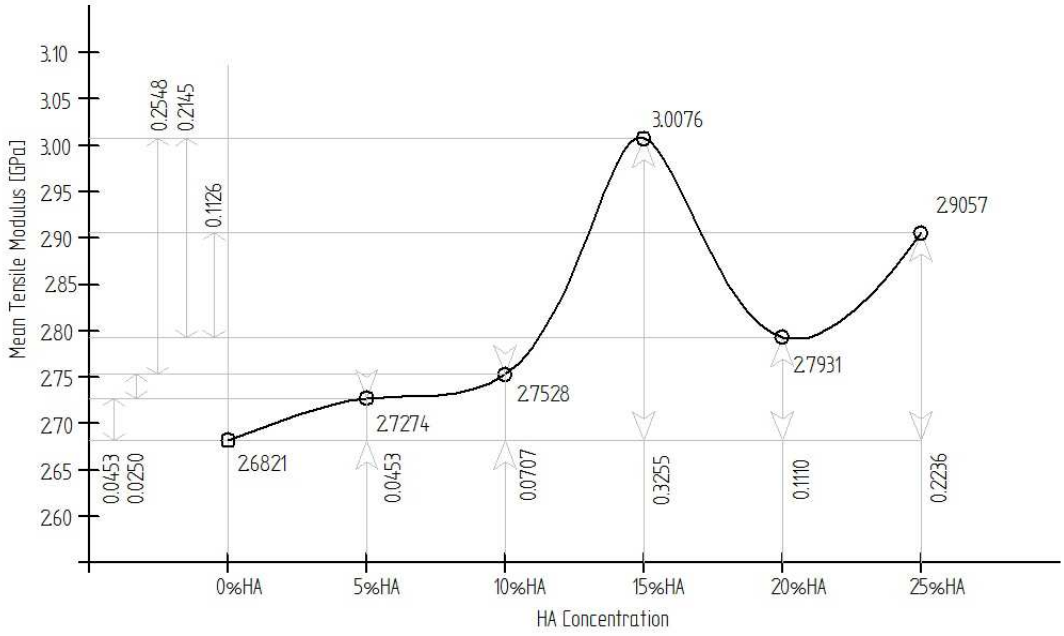


Figure 34: Relationship of mean tensile modulus to increased HA concentration

Deriving an interpolation equation was not easy, with conformance tests showing small R-squared values *[0.306 maximum]*, suggesting that a best-fit cubic curve did not represent a very accurate interpolation. This was borne out in the observation, *post-hoc*, that the interpolated calculations provided a rising tensile modulus that peaks at 20 percent HA, in contradiction to the measured values.

The peak tensile modulus value at the 15 percent HA concentration, as highlighted above, is further supported in the observation, statistically, that the tensile modulus of the 15 percent samples was significantly different to those of

both pure PMMA *[p = 0.001]* and the 10 percent HA samples *[p = 0.018]*.

	0%	5%	10%	15%	20%	25%
0%						
5%	1.000					
10%	1.000	1.000				
15%	***0.001***	0.053	***0.018***			
20%	1.000	1.000	1.000	0.073		
25%	0.053	0.248	0.554	1.000	1.000	

Table 25: Summarised comparative p-values for tensile modulus

5.6 SHEAR STRENGTH TEST RESULTS

If two equal-in-magnitude but opposite-in-direction, parallel but non-collinear forces are applied to an object, there will be a tendency for one part of the body to slide over or shear from the other part. Shear strength is a descriptive term for a material's maximum ability to withstand this loading scenario (Ryder, 1974:24). In the application of prostheses, shear stress would be in evidence if a small, flat object were to load the prosthetic as if it were trying to penetrate (this is known as punch-shear). During bending (which is an inevitable load scenario in the case of prosthetics), shear stress manifests itself in plane with the axis of the material being bent. This is known as transverse shear loading (Ryder, 1974:24).

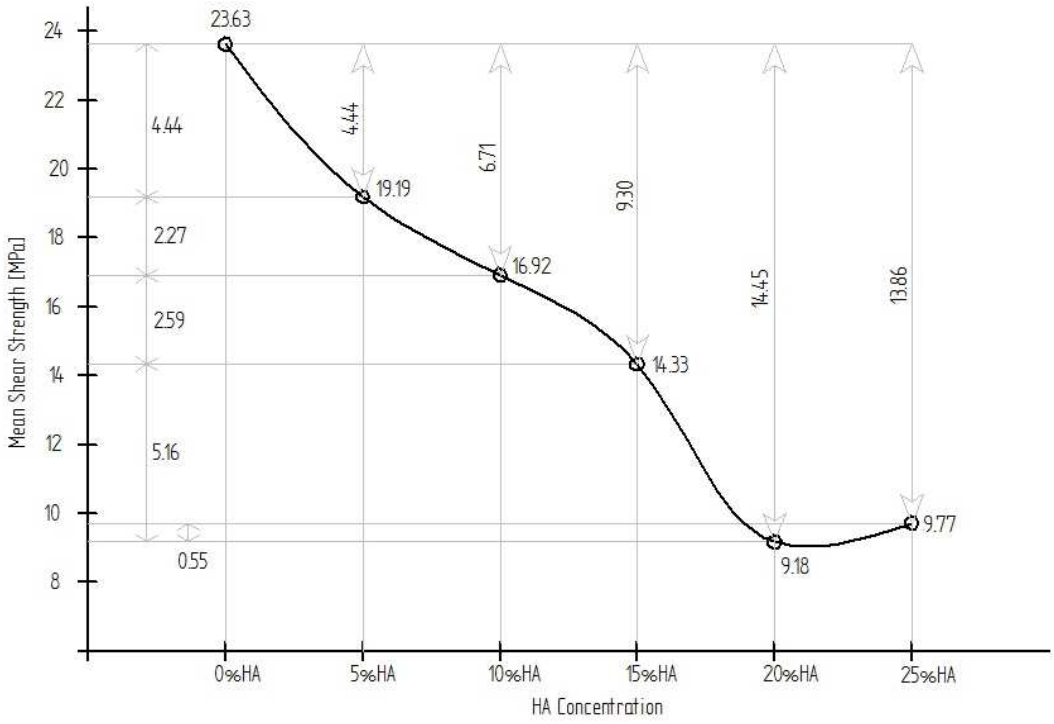


Figure 35: Relationship of mean shear strength to increased HA concentration

Figure 35, above, indicates a clear trend of declining shear strength with increasing HA percentage. This observation was described previously, in reference to ***Figure 27*** *[See Section 4.3.4]*, in which the scatter plot suggested a linear mathematical relationship between the dependent variable (shear strength) and the independent (HA concentration).

In ***Table 26***, below, it may be observed that the linear decrease in shear strength assumes statistical importance at the 15 percent HA concentration. All concentrations of HA above 15 percent are statistically weaker, in terms of shear strength, than pure PMMA *[p = 0.000 – 0.004]*, and samples having greater than 15 percent HA were demonstrated ,furthermore,to be statistically weaker than even lower concentration HA samples (i.e. 5 percent- and 10 percent HA) *[p = 0.002 – 0.044]*.

	0%	5%	10%	15%	20%	25%
0%						
5%	0.784					
10%	0.075	1.000				
15%	***0.004***	0.523	1.000			
20%	***0.000***	***0.002***	***0.023***	0.389		
25%	***0.000***	***0.003***	***0.044***	0.067	1.000	

Table 26: Summarised comparative p-values for shear strength

As has been described previously, with reference to tensile strength and compressive strength, the CV values for the 20 percent HA *[58.8]* and 25 percent HA *[43.2]* samples were notably greater than those of pure PMMA *[8.13]* and lower HA concentration samples *[3. 54 – 29.2]*. This would suggest that composites containing such concentrations of HA would demonstrate unacceptably low levels of clinical reliability.

5.7 THE POOLED MECHANICAL TEST RESULTS

Pooling of the mean strength and modulus results provides a snapshot view of the trends and idiosyncrasies associated with the respective PMMA/HA composites, relative to pure PMMA. The aim of this study is to characterise composites of varying HA concentrations, with a view to identifying an HA concentration that would represent an optimal compromise of the strength and

modulus properties of pure PMMA and the biological tolerability and bioactivity of HA.

Comparison of the four mechanical strength properties, as reflected in ***Figure 36***, below, shows a clear downward trend as in all four mean strengths as HA concentration is increased. It is to be assumed, therefore, that any addition of HA to pure PMMA, to form a composite, would necessitate a corresponding loss of flexural, compressive, tensile and shear strengths. Such inevitable loss of strength would need, however, to be evaluated, and offset, against the anticipated gains in terms of bioactivity and integration of the prosthesis derived through incorporation of HA into the PMMA matrix.

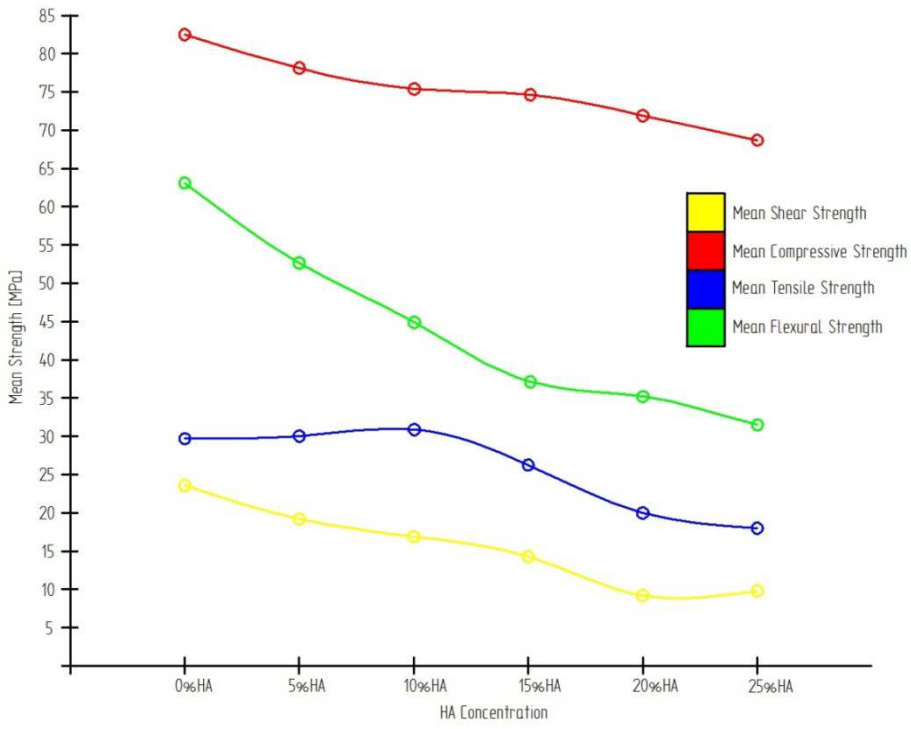


Figure 36: Relationship of mean strengths to increased HA concentration

The comparison of the compressive, flexural and tensile moduli reveals more interesting results. As can be observed in ***Figure 37***, below, the impact of the addition of HA to PMMA on the three moduli under investigation is more varied

and mathematically more complex. The concentration of HA which results in a composite having modulus values most akin to those of pure PMMA is 15 percent (albeit that this concentration displays and increased tensile modulus). Concentrations of less than 15 percent HA display a notably, although not statistically significant, reduction of the compressive modulus, and those above, and increased flexural modulus. The 15 percent HA composite would, therefore, represent a focus for the more precise determination of an optimal concentration

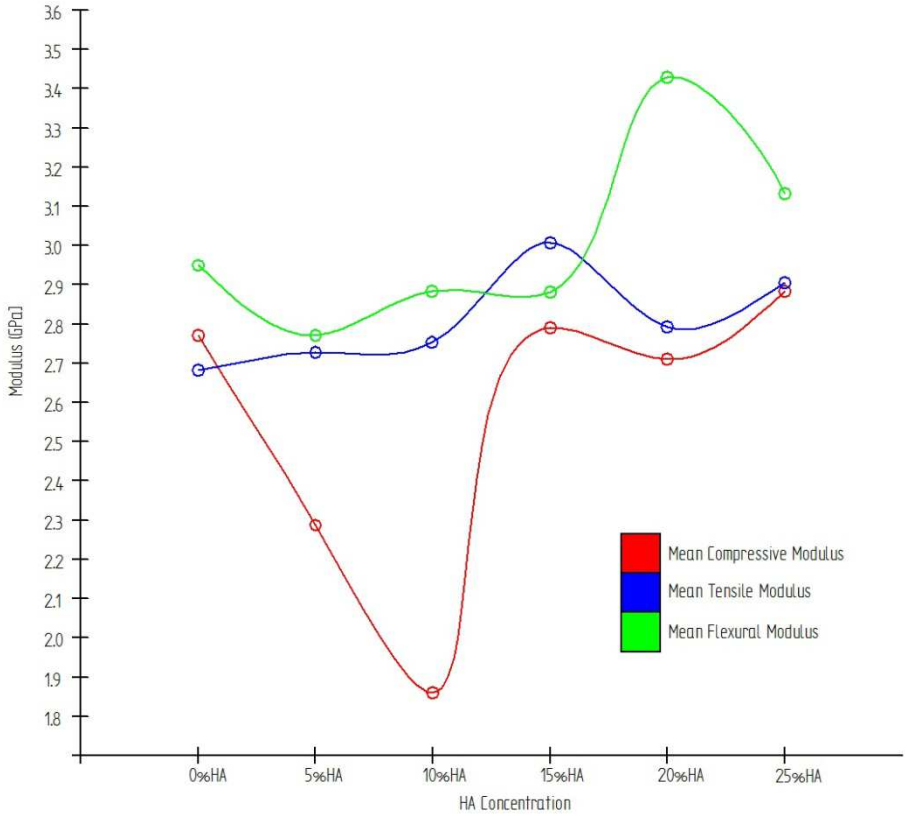


Figure 37: Relationship of mean moduli to increased HA concentration

An alternative view, arises from the observation that whereas the means of the measurements of respective strengths show definable trends that are easily characterised mathematically, the calculations of respective moduli have been consistently more varied, and their mathematical definition considerably more

difficulty, if at all. This alternative view would contend that the modulus results are 'random', and would offer the following mathematical argument in support of the contention:

Strength, or stress, for tensile and compressive loads is calculated as follows:

$$\sigma = \frac{F}{A}$$

where: σ = strength (or stress), measured in MPa (N/mm^2)
F = the load applied axially along the specimen, in N
A = the cross-sectional area of the specimen, measured in mm^2;

Strain, for tensile and compressive loads, is calculated as follows:

$$\varepsilon = \frac{\Delta L}{L}$$

where: ε = strain, which is a dimensionless number
ΔL = the change in length measured axially along the specimen as it is loaded, measured in mm
L = the original length of the specimen before loading, measured in mm;

The modulus of elasticity (in compression or tension) is defined as stress over strain:

$$E = \frac{\sigma}{\varepsilon}$$

Where: E = Modulus of elasticity in tension or compression, as

the case may be, measured in N/mm^2 or MPa, which is by convention converted to GPa.

As stated above, the ‘strength’ variable has behaved in a manner that has allowed for the easy identification of trend, and so the ‘strength’ component of the modulus equation may be considered to represent reliable data. This would suggest that the ‘strain’ value would represent the possible confounder towards seemingly random results. ‘Strain’ is calculated by dividing the change in length of a specimen, by the original length of the specimen, so it would therefore be reasonable to investigate these specific measurements as a possible source of the apparent ‘randomness’.

The change in length (***ΔL***) component is measured by the extensometer illustrated in ***Figure 5*** of Chapter 3. It is a device with the necessary resolving power to absolutely accurately measure in units of 0.007mm (or 7µm). For purposes of such measurement, the original length of the specimen is not calculated as the total length of the specimen, nor the distance between the jaws of the testing apparatus, but rather as the distance between the attachment points of the extensometer. This is rigidly set when fitting the extensometer to the specimen. The extensometer has a mechanical stop that is utilised when it is fixed by means of spring loaded blades to the specimen. As such it is a non-adjustable, non-changing dimension and is set at 25.40mm.

Reviewing the above, it would seem, as the components of strength have proven characterised results, and the original length component of Strain is fixed ,that the one element that could be contributing to the disappointing modulus results is the change in length, *ΔL*.

The resolving power of the extensometer was within the requirements of the respective testing standards; the attachment method also complied to the standard and is well-proven; and the extensometer employed in measurement was calibrated and had the requisite certification. This therefore would

reasonably suggest that the measurements, in themselves, were accurate. In turn, this would suggest that the sample *itself* may, in fact, be at issue. In other words, the elongation behaviour of the material under investigation was not as it ought to have been. For mathematically-definable extension to take place, the material must, necessarily, elongate in a manner that can be mathematically characterised.

The material, PMMA, is composed of two parts, a powdered solid and a liquid monomer. When these constituents are mixed in a precise ratio, the monomer reacts with the powder, promoting polymerisation. The quality of this process is dependent on the effectiveness of the mixing, or the homogeneity of the distribution of catalyst to powder. If this mixture were not properly homogenous, then it would be correspondingly likely to display variations in the completeness of the polymerisation process and, with this, variability in its mechanical performance.

The further addition of HA, to form a composite, yields a second variable in the form of variable particle size. This mix quality would, be argued to affect the elongation behavior, as described in the previous paragraph, as well as creating (through variations in particle size) localised areas in which elongation behaviour may be less than consistent. The suggestions that the methodology utilised in this study might have yielded a less-than-‘homogenous dough’, and that the mechanical properties of samples more appropriately mixed would yield different results, find support in existing literature that came to the researcher’s attention after the formulation of the methodology and the implementation of this study.

Lidgren, Bodelind and Möller (1987) have proposed that composite cements, such as are the PMMA/HA composites investigated in this study, should be mixed mechanically and under vacuum. Under vacuum-mixing conditions the porosity of PMMA is reduced (Alkire, Dabezies and Hastings, 1987) and mechanical strength of the composite is increased (Jasty *et al.*, 1990).

CHAPTER SIX: THE CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

6.1.1 INTRODUCTION

This study attempted to provide an understanding of the exothermic polymerisation cycle characteristics and mechanical properties of a range of PMMA/HA composites. The implementation of the study, the recording of results and statistical analysis of the data have suggested the following conclusions with respect to the characterisation of PMMA/HA composites in the 5 percent to 25 percent HA range:

6.1.2 EXOTHERMIC POLYMERISATION TEST RESULTS

The test results of exothermic polymerisation cycle characteristics revealed that while the mean maximum exothermic temperature for all six groups were in excess of 100˚C, and therefore not ideal for extensive *in situ* repairs, the addition of HA appeared to decrease the maximum exothermic temperatures. The greatest individual drop was seen to occur when evaluating pure PMMA against a five percent HA composite: this resulted in a 9.8℃ reduction from 120.8℃ to 111℃. Further increases in the HA propo rtion to 25 percent resulted in an 18℃ reduction from 120.8℃ to 102.8℃, when compared to pure PMMA. The clinical usefulness of this observation is an issue of debate, but the gain in working time created when HA is added would suggest a positive benefit to the surgeon attempting to shape an *in situ* prosthesis.

6.1.3 FLEXURAL TEST RESULTS

The flexural test results for the PMMA/HA composites showed that there was a significant reduction in flexural strength in the range between zero percent HA (pure PMMA) and 15 percent HA *[p = 0.000 – 0.034]*. However, there was found to be no significant flexural strength difference between the 15 percent HA and 25 percent HA composites *[p = 0.163 – 1.000]*. This would suggest that increasing the HA percentage beyond 15 percent does not significantly alter the mean flexural strength of the PMMA/HA composite It was noted that the maximal flexural strength was in pure PMMA, at a level of 63.11MPa.

Comparison of the results of the flexural modulus for the various PMMA/HA composites showed there was no statistically significant difference between the six groups, and the addition of HA therefore has no significant effect on flexural modulus. The greatest flexural modulus was noted to exist as 20 percent HA.

6.1.4 COMPRESSIVE TEST RESULTS

Maximal compressive strength was noted at the zero percent HA level (pure PMMA). Whilst there was a notable trend toward a steady decrease in compressive strength as the HA percentage increased, this decrease only achieved statistical significance at, and above, a 20 percent HA concentration *[p = 0.001 – 0.022]*.

As was the case in the testing of flexural modulus, there were no statistically significant differences between the range of compressive modulus samples. It is noted, however, that whilst the compressive modulus of the 15 percent- to 25 percent HA samples was of similar value to that of pure PMMA *[within a range of 2.7100 – 2.8884 GPa]*, lower concentrations of HA than 15 percent notably reduced the compressive modulus *[5%HA: 2.2874GPa; 10%HA: 1.8607GPa (10%)]*.

6.1.5 TENSILE TEST RESULTS

The tensile strength test results for the PMMA/HA specimens showed that there was no significant difference between pure PMMA and composites containing up to 15 percent HA. There was, however a significant difference between the 20 percent- and 25 percent HA composites and those of lower HA concentration. The lower 75th percentile tensile strength trend confirmed an increased failure risk as HA concentration was increased above 10 percent towards 25 percent. Caution would be advised if concentrations above 15 percent HA are to be used, in order to avoid a reduced tensile strength range and difficulties of ensuring homogeneity of the composite. In terms of tensile strength, the best compromise of strength and bioactivity was observed at a concentration of 10% HA.

The analysis of tensile modulus revealed that there was a significant difference between 15 percent HA composites and, respectively, pure PMMA and the 10 percent HA composite. This was further confirmed by increasing tensile modulus trend, peaking at 15 percent HA.

6.1.6 SHEAR STRENGTH TEST RESULTS

Shear strength was noted to decrease with HA percentage, following a linear trend. Significant differences between the means of some sample groups were noted: the 15 percent HA composite displayed statistically significantly less shear strength than pure PMMA, and the 20 percent- and 25 percent HA composites displayed significant reduced shear strength against both pure PMMA and composites of less than 10 percent HA. This suggests that increasing HA concentration beyond 20 percent would have a significantly adverse effect on the shear strength of the resultant composite.

6.2 RECOMMENDATIONS

1. This study has revealed that the addition of HA to pure PMMA negatively affects the mechanical strength measured in compression, bending or shear. As such, it may be argued that no HA should be added. The results of tensile strength, which peaked at an HA concentration of ten percent, were the only exception.

   Modulus testing revealed a different picture where moduli in tensile, compression and flexure all showed a gentle increase with the addition of increasing amounts of HA. For tensile modulus the peak value was noted at 15 percent; for compressive modulus at 25 percent; and for flexural modulus the peak at 25 percent HA.

   The researcher therefore, recommends that the best compromise across all properties (mechanical and thermal) should be based upon the nature of the prosthesis, and its respective requirement for strength, stiffness, size, thickness and curing time.

   By way of example, it is the opinion of the researcher that strength would be less critical than stiffness in such applications as cranial bone replacement prosthetics, due to the fact that, in the adult, loading of the cranium (or prosthesis) with sufficient force to cause significant damage is generally avoided. On the other hand, in such contexts in which it would be required of a prosthesis to be very thin, or to feature thin design elements, increased moduli in tension, compression and flexure would allow a greater degree of design leeway. This would also be true in those cases in which the maintenance of geometrical shape is very important.

   Finally, the bioactivity advantages to be derived by the addition of HA to a composite cannot be underestimated. It is thus recommended that

PMMA/HA composite materials with 10 – 15 percent HA be considered for use in small areas, such as would occur in such dental contexts as implants, , due to the advantages in the exothermic polymerisation cycle, flexural modulus, compressive modulus, tensile modulus and tensile strength. The decrease in compressive, flexural and shear strength are offset against the bioactivity gained when adding HA to the PMMA. This study was, unfortunately, too preliminary and limited to provide insight into the potential of using PMMA/HA composites as a means of achieving bioactive bonding to bone in such contexts as cranial prostheses. The high exothermic maximum temperature would certainly suggest that such prosthesis manufacture would not be possible *in situ*.

2. The implementation of this study highlighted a number of limitations of the current scope and design, and raised some useful insights into possible future research towards confirmation and extension of the results of this study. These include:

- The number of test samples should be increased to 30 each, which would increase the power of statistical conclusions;
- There is a possibility that homogeneity of mixing may have confounded the modulus result ensures. A more refined methodology of mixing that ensures maximal homogeneity should be investigated and applied. In this respect, the researcher would suggest the investigation of mechanical mixing under vacuum, as originally proposed by Lidgren *et al.* (1987), and as discussed in Section 5.7, above.
- The data collected is insufficiently accurate for design purposes. A more refined methodology, using more sensitive standards, and applied to a greater number of samples would increase the accuracy of the necessarily preliminary results represented by this study, and allow for more definitive conclusions;

- Shear modulus testing was not conducted in this study due to budgetary limitations. For the sake of completeness, this property ought also to be investigated.
- The effect of the HA variation on impact resistance is another important property that should be investigated.

3. The analysis of bioactivity variation with changing HA percentages was beyond the scope of this study. Since bioactivity is the most important assumed advantage of the addition of HA, the more accurate description of this outcome should be pursued. The optimal HA percentage would see this bioactivity feature assuming prime importance, since PMMA/HA composites in any form are understood to exceed the strength and stiffness of natural bone (Shi, 2006:7)

4. A further important property that ought to be investigated would be the effect of increasing concentrations of HA on the degradation of the composite components. Currently, prostheses, of all descriptions, are understood to not be 'lifetime' items, sometimes lasting as little as five years before requiring replacement. Mechanisms for prolonging the 'life' of a prosthetic would hold a number of advantages, not least of which are surgery avoidance and the attendant cost-saving.

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G0E: 0% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	32	32	34	31	32	32.2	1.33	0.04
60	36	36	40	35	36	36.6	9.71	0.27
70	37	38	42	38	38	38.6	38.6	0.34
80	41	41	50	41	41	42.8	15.61	0.36
90	47	47	66	52	48	52.0	17.12	0.33
100	61	71	112	72	71	77.4	20.01	0.26
110	103	109	119	113	110	110.8	5.24	0.05
120	114	112	121	117	113	115.4	3.76	0.03
130	117	119	124	118	120	119.6	4.89	0.04
140	119	119	125	119	121	120.6	8.26	0.07
150	117	118	126	117	121	119.8	12.80	0.11
180	113	112	126	115	121	117.4	26.10	0.22
210	108	111	122	113	120	114.8	39.23	0.34
240	104	108	118	111	117	111.6	52.69	0.47
270	100	105	114	108	114	108.2	66.27	0.61

G5E: 5% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	31	31	31	31	31	31	0.41	0.01
60	34	34	35	33	33	33.8	10.72	0.32
70	35	36	37	34	34	35.2	14.25	0.40
80	37	38	41	35	35	37.2	17.61	0.47
90	39	39	42	37	37	38.8	20.98	0.54
100	43	42	43	40	40	41.6	23.88	0.57
110	50	46	52	45	44	47.4	25.74	0.54
120	76	63	76	64	64	68.6	21.84	0.32
130	101	100	101	94	92	97.6	13.77	0.14
140	104	105	112	111	11	88.6	44.22	0.50
150	107	107	113	112	113	110.4	16.41	0.15
180	108	108	112	112	113	110.6	28.41	0.26
210	107	109	110	111	113	110	40.87	0.37
240	107	109	110	109	112	109.4	53.34	0.49
270	104	107	107	107	109	106.8	66.65	0.62

G10E: 10% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	31	31	31	31	31	31	0.41	0.01
60	32	32	32	32	32	32	11.43	0.36
70	32	32	33	32	32	32.2	15.44	0.48
80	33	33	34	33	33	33.2	19.11	0.58
90	33	33	34	33	33	33.2	23.19	0.70
100	34	34	34	34	34	34	26.94	0.79
110	35	35	35	34	35	34.8	30.70	0.88
120	36	36	36	36	36	36	34.29	0.95
130	37	38	36	37	37	37	37.97	1.03
140	39	39	38	38	39	38.6	41.40	1.07
150	43	42	39	41	42	41.4	44.36	1.07
180	69	69	66	67	67	67.6	45.90	0.68
210	110	115	109	107	106	109.4	41.19	0.38
240	107	110	106	104	104	106.2	54.67	0.51
270	104	106	103	101	100	102.8	68.29	0.66

G15E: 15% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	30	30	30	30	30	30	0.00	0.00
60	33	32	31	32	32	32	11.45	0.36
70	34	33	31	33	33	32.8	15.22	0.46
80	37	34	32	35	35	34.6	18.61	0.54
90	40	37	39	36	37	37.8	21.36	0.57
100	46	42	50	43	44	45	22.63	0.50
110	61	50	84	51	56	60.4	23.76	0.39
120	94	84	101	85	89	90.6	13.55	0.15
130	103	100	106	99	101	101.8	11.78	0.12
140	105	100	108	104	105	104.4	14.76	0.14
150	106	104	107	108	107	106.4	17.85	0.17
180	104	107	105	107	108	106.2	30.16	0.28
210	99	103	104	106	107	103.8	43.45	0.42
240	96	100	100	104	105	101	56.84	0.56
270	95	98	98	101	104	99.2	69.80	0.70

G20E: 20% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	30	30	30	30	30	30	0.00	0.00
60	32	31	31	31	32	31.4	11.69	0.37
70	32	32	32	32	33	32.2	15.44	0.48
80	33	32	32	33	33	32.6	19.36	0.59
90	33	33	33	34	35	33.6	23.04	0.69
100	33	33	34	35	36	34.2	26.89	0.79
110	34	35	34	36	36	35	30.63	0.88
120	36	37	35	38	38	36.8	33.99	0.92
130	37	38	37	39	41	38.4	37.43	0.97
140	38	42	38	42	45	41	40.51	0.99
150	41	45	40	46	52	44.8	43.16	0.96
180	80	91	72	91	100	86.8	39.28	0.45
210	103	106	104	106	108	105.4	42.74	0.41
240	105	107	105	107	107	106.2	54.63	0.51
270	101	105	102	104	103	103	68.19	0.66

G25E: 25% HA

Time *[s]*	SPECIMEN NUMBER *[Temperature in ℃]*					Mean	SD	CV
	1	2	3	4	5			
30	31	31	32	31	31	31.2	0.63	0.02
60	33	34	33	32	32	32.8	11.13	0.34
70	35	36	35	33	33	34.4	14.58	0.42
80	37	38	37	34	34	36	18.04	0.50
90	40	42	39	38	38	39.4	20.71	0.53
100	45	50	42	42	42	44.2	22.99	0.52
110	53	60	49	51	54	53.4	23.40	0.44
120	68	75	64	67	70	68.8	21.22	0.31
130	89	100	85	82	87	88.6	17.99	0.20
140	94	102	89	94	92	94.2	19.19	0.20
150	97	105	98	99	97	99.2	20.95	0.21
180	99	106	102	104	103	102.8	31.60	0.31
210	96	97	100	104	102	99.8	45.09	0.45
240	94	92	94	100	97	95.4	59.10	0.62
270	89	89	89	95	92	90.8	73.20	0.81

G0F: 0% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	9.70	2.05	14.88	35.00	59.15	2.92
2	7.10	2.05	15.23	35.00	56.84	2.22
3	11.25	2.00	15.18	35.00	67.47	2.64
4	9.80	2.05	15.23	35.00	72.61	3.01
5	6.00	2.03	14.70	35.00	59.47	3.96

G5F: 5% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	8.20	2.02	14.94	35.00	53.33	2.62
2	10.00	2.06	15.12	35.00	57.78	2.65
3	8.40	2.02	15.24	35.00	40.49	2.70
4	10.60	1.98	15.14	35.00	54.10	2.83
5	7.30	2.00	14.98	35.00	57.53	3.04

G10F: 10% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	8.10	2.04	14.95	35.00	38.59	2.81
2	7.80	2.01	14.99	35.00	41.59	3.33
3	8.70	2.06	15.07	35.00	39.98	2.78
4	7.40	1.98	15.03	35.00	60.12	3.11
5	7.70	1.96	15.08	35.00	44.10	2.39

G15F: 15% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	8.40	1.97	15.22	35.00	45.31	3.32
2	8.20	1.98	15.10	35.00	32.16	3.14
3	7.70	2.02	15.02	35.00	29.64	2.17
4	8.20	2.04	15.13	35.00	40.39	2.68
5	9.80	2.00	14.89	35.00	38.27	3.09

G20F: 20% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	9.00	2.00	14.88	35.00	32.41	3.51
2	8.60	2.00	14.95	35.00	30.94	3.74
3	6.60	2.04	15.02	35.00	38.47	3.30
4	8.70	1.98	15.12	35.00	37.88	3.42
5	7.80	1.97	15.22	35.00	36.24	3.07

G25F: 25 % HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Flexural Strength *[MPa]*	Flexural modulus *[GPa]*
1	7.00	1.99	14.97	35.00	34.43	2.92
2	8.70	2.06	15.30	35.00	27.57	2.69
3	10.30	1.96	15.06	35.00	33.01	3.69
4	9.70	2.00	14.94	35.00	43.76	3.67
5	9.40	2.01	14.88	35.00	18.66	2.69

G0C: 0% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	4.60	2.05	12.95	18.10	2.67	2.67
2	6.70	2.05	13.00	18.10	1.69	1.69
3	13.00	2.05	12.85	18.10	3.14	3.14
4	16.50	2.05	12.93	18.10	3.20	3.20
5	4.30	2.05	12.92	18.10	3.16	3.16

G5C: 5% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	3.60	2.05	12.95	18.10	1.50	1.50
2	3.70	2.05	12.92	18.10	2.74	2.74
3	19.70	2.05	12.98	18.10	3.17	3.17
4	0.00	2.03	12.70	18.10	2.01	2.01
5	19.11	2.10	12.95	18.10	2.02	2.02

G10C: 10% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	10.60	2.07	13.05	18.10	1.08	1.08
2	9.30	2.02	12.95	18.10	0.72	0.72
3	3.60	2.05	12.93	18.10	2.46	2.46
4	13.70	2.05	12.97	18.10	3.02	3.02
5	3.70	2.02	12.87	18.10	1.72	1.72

G15C: 15% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	3.50	2.07	12.90	18.10	1.93	1.93
2	23.00	2.15	13.07	18.10	3.90	3.90
3	8.10	2.10	13.10	18.10	1.67	1.67
4	7.20	2.10	12.78	18.10	3.08	3.08
5	8.00	2.15	12.90	18.10	3.41	3.41

G20C: 20% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	13.30	2.05	13.00	18.10	3.71	3.71
2	14.00	2.07	13.22	18.10	2.84	2.84
3	3.70	2.07	13.10	18.10	1.97	1.97
4	14.40	2.05	13.17	18.10	2.64	2.64
5	13.70	2.05	13.10	18.10	2.74	2.74

G25C: 25% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Compressive Strength *[GPa]*	Mean Compressive Modulus *[GPa]*
1	3.90	2.05	12.73	18.10	2.83	2.83
2	3.30	2.07	13.00	18.10	2.68	2.68
3	7.20	2.08	13.23	18.10	3.68	3.68
4	10.90	2.08	13.02	18.10	2.13	2.13
5	3.60	2.02	12.77	18.10	3.13	3.13

G0T: 0% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	80.00	2.00	12.82	25.00	2.64	34.09
2	59.00	1.98	13.10	25.00	2.49	23.46
3	79.33	2.02	12.80	25.00	2.81	36.33
4	89.00	2.05	13.25	25.00	2.60	31.61
5	81.40	2.00	13.02	25.00	2.87	22.13

G5T: 5% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	71.00	2.07	12.92	25.00	2.84	33.20
2	82.20	2.05	13.08	25.00	2.72	33.87
3	65.40	2.10	13.35	25.00	2.70	29.06
4	61.00	2.10	13.23	25.00	2.74	28.45
5	87.40	2.10	13.43	25.00	2.64	25.66

G10T: 10% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	51.00	2.10	13.15	25.00	2.76	30.43
2	72.10	2.10	13.68	25.00	2.96	27.00
3	65.00	2.08	12.98	25.00	2.57	32.30
4	81.60	2.10	13.22	25.00	2.79	31.98
5	66.30	2.10	13.05	25.00	2.68	30.99

G15T: 15% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	62.30	2.10	13.30	25.00	3.05	23.37
2	63.90	2.10	13.25	25.00	3.06	26.77
3	73.70	2.10	13.12	25.00	2.95	24.06
4	84.00	2.10	13.05	25.00	3.10	29.46
5	60.90	2.10	13.18	25.00	2.88	27.69

G20T: 20% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	60.70	2.10	12.92	25.00	2.71	22.20
2	55.20	2.08	13.10	25.00	2.85	24.47
3	68.00	2.10	12.88	25.00	2.75	14.51
4	59.10	2.10	13.08	25.00	2.86	24.57
5	76.20	2.07	13.00	25.00	2.80	14.27

G25T: 25% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Tensile Strength *[GPa]*	UTS *[MPa]*
1	51.20	2.00	12.82	25.00	3.05	23.01
2	50.10	1.98	13.10	25.00	2.84	13.36
3	45.90	2.02	12.80	25.00	2.83	16.51
4	50.10	2.05	13.25	25.00	2.96	20.15
5	41.20	2.00	13.02	25.00	2.80	17.09

G0S: 0% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	12.00	3.02	12.03	25.00	23.72
2	10.32	3.04	11.90	25.00	20.79
3	9.98	3.04	11.96	25.00	23.79
4	9.99	2.98	12.00	25.00	23.63
5	16.22	3.02	12.05	25.00	26.21

G5S: 5% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	10.24	2.99	12.10	25.00	19.87
2	12.56	2.98	12.06	25.00	20.75
3	9.33	2.96	12.15	25.00	20.17
4	15.02	3.02	12.16	25.00	17.61
5	12.96	2.97	12.08	25.00	17.55

G10S: 10% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	12.65	3.02	12.06	25.00	17.58
2	10.22	3.04	11.99	25.00	17.53
3	9.08	3.01	11.96	25.00	16.70
4	9.06	3.00	11.98	25.00	16.49
5	12.56	2.99	11.97	25.00	16.30

G15S: 15% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	8.33	3.00	11.97	25.00	6.96
2	12.25	3.01	12.00	25.00	16.88
3	13.08	3.00	12.00	25.00	15.97
4	15.74	2.98	12.03	25.00	15.00
5	12.36	2.95	12.00	25.00	16.85

G20S: 20% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	9.68	3.06	11.96	25.00	16.15
2	9.84	3.01	11.99	25.00	7.41
3	9.26	3.04	11.94	25.00	3.21
4	12.22	2.99	11.90	25.00	5.75
5	12.85	3.00	12.00	25.00	13.36

G25S: 25% HA

Sample Number	Preload *[N]*	Thickness *[mm]*	Breadth *[mm]*	Span *[mm]*	Maximum Shear Strength *[MPa]*
1	13.84	2.97	12.01	25.00	3.05
2	11.26	3.03	11.98	25.00	8.12
3	14.23	3.01	11.97	25.00	11.70
4	11.93	2.99	11.99	25.00	12.71
5	9.36	3.02	12.00	25.00	13.03