



**SYNTHESIS OF NANOCOMPOSITES WITH NANO-TiO₂ PARTICLES AND THEIR
APPLICATIONS AS DENTAL MATERIALS**

**By
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ABSTRACT

A study of the modification of dental nanocomposites with nanosized fillers is presented. The incorporation of TiO₂ (titania) nanoparticles, via a silane chemical bond, to a standard dental acrylic resin matrix was explored to determine whether there was an increase in the wear resistance, flexural strength and surface hardness properties of the dental nanocomposites. The principal aim of this study was to synthesize dental nanocomposites with different sizes, treated, nano-TiO₂ fillers in urethane dimethacrylate (UDMA) for potential application in posterior restoration and to evaluate their mechanical properties.

Treatment of the nano-TiO₂ particles was carried out with a silane coupling agent, 3-(methacryloyloxy)propyltrimethoxysilane (MPTMS), to improve bonding between the nano-TiO₂ particles and acrylic matrix (UDMA), and reduce agglomeration of the nano-TiO₂. Characterisation of products was carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fourier transform infrared spectroscopy (FTIR). TEM results were used to compare the particle size distributions of untreated TiO₂ and treated TiO₂ under various experimental conditions in an ethanol solvent, while SEM images showed the adhesion between the matrix (UDMA) and the nano-TiO₂. FTIR was used to show the qualitative composition of untreated TiO₂ and treated TiO₂.

Eighteen groups of experimental dental nanocomposites were evaluated. Each group contained different average particle sizes of nano-TiO₂ (filler): 5 nm, 21 nm and 80 nm. Each particle size category was treated with three different concentrations of the silane, (MPTMS): 2.5, 10 and 30 wt %. Samples were prepared by mixing the monomer resin matrix of UDMA and nano-TiO₂ particles. For comparison, a commercially available dental resin was reinforced with untreated and treated nano-TiO₂ particle sizes 5, 21 and 80 nm.

Wear resistance, flexural strength and surface hardness of TiO₂ nanocomposites treated with 2.5 wt % MPTMS were significantly higher compared to those treated with 10 and 30 wt% MPTMS. The nanocomposites with 5 nm TiO₂ had higher wear loss, lower flexural strength and lower surface hardness values compared to those with 21 nm and 80 nm TiO₂. Statistical analysis showed that the effect of the concentrations of MPTMS on wear resistance and surface hardness of specimens was significant ($p < 0.001$), which is less than 0.05, while the effect of the concentration of MPTMS on flexural strength was statistically not significant, ($p = 0.02$). Control composites reinforced with treated 80 nm TiO₂ particles had much better mechanical properties than any of the other specimens. It was concluded that the most available commercial product for dental restorations could be improved by the addition of nano-TiO₂ with relatively large particle size.

KEYWORDS

Wear resistance

Nano-TiO₂ particles

Dental nanocomposites

Dental restoration

Coupling agent

Flexural strength

Microhardness

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DEDICATION

In the name of Allah the beneficent and the merciful, all praise and thanks is due to Allah for giving me the ability and health to complete my study successfully.


This study is dedicated to the greatest power, through which all things are made possible, my creator, ALLAH 'TAALA (GOD ).

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DEFINITION OF KEY TERMS

- **Nano-TiO₂ particles:** titanium filler particles of less than 100 nanometer in diameter exhibiting new or enhanced size-dependent properties compared with microparticles of the same substance (Roy *et al.*, 2005).
- **Nanocomposites:** materials incorporating filler nanoparticles into a resin matrix of standard material; or a material that results from the intimate mixture of two or more nano phase substances (Chau *et al.*, 2008).
- **Dental resin composite:** a material consisting of two or more components. Typically, a dental resin composite contains organic, inorganic filler and coupling agent incorporated into a system that would induce polymerization, used as dental restoration materials (Cramer *et al.*, 2011).
- **Dental resin matrix:** an organic material (monomer), used as a main ingredient in dental composites (Anusavice, 2003).
- **Filler:** an inorganic material (particles) added to improve the properties of composites material (Lutz *et al.*, 1983).
- **Coupling agent:** a chemical substance capable of reacting with both the filler particle and the resin matrix of a composite material. It may also bind fibres or inorganic fillers to organic resins, to promote or form a stronger bond at the interface (Novais *et al.*, 2011).
- **SR Adoro®:** a microfilled, light/heat curing veneering indirect composite for partial and full coverage veneers, introduced by Ivoclar Vivadent (Zandinejad *et al.*, 2006).

- **Wear:** Erosion or sideways displacement of material from its derivative and original position, on a solid surface as a result of the action of another surface. It is correlated to interactions between surfaces and more particularly the removal and deformation of material on its surface as a result of mechanical action of the opposite surface (Williams, 2005).
- **Pin-on-disc:** The pin-on-disc test has proved useful in providing a simple friction and wear test for low friction coatings such as diamond like carbon coatings on valve train. Consisting of a stationary pin under an applied load in contact with a rotating disc, the tribometer pin can have any shape to simulate a specific contact. Spherical tips are often used to simplify the contact geometry. The friction coefficient is determined by the ratio of the frictional force to the loading force on the pin (Bressan, 2008).

ABBREVIATIONS

ASMI	-	American society for metals international
Bis-GMA	-	Bisphenol-A glycidyl methacrylate
CQ	-	Camphorquinone
DMAEMA	-	2-(Dimethylamino)ethylmethacrylate
EDS	-	Energy dispersive spectrometry
FTIR	-	Fourier transform infra red spectroscopy
FRC	-	Fiber reinforced composite
MPTMS	-	3-(methacryloyloxy)propyltrimethoxysilane
MPa	-	Mega Pascal
Nano-TiO ₂	-	Nanoparticles of titanium dioxide
PFM	-	Porcelain fused to metal
PMMA	-	Poly(methylmethacrylate)
SEM	-	Scanning electron microscopy
TEM	-	Transmission electron microscopy
TEGDMA	-	Triethyleneglycol dimethacrylate
UDMA	-	Urethane dimethacrylate
VHN	-	Vickers hardness number
γ-MPS	-	γ-(methacryloxy)propyltrimethoxysilane

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The ultimate goal of dentistry and dental technology is to maintain or improve the quality of life of the dental patient. This aspiration can be realised by preventing disease, relieving pain, improving mastication efficiency, enhancing speech and improving appearance. To achieve many of these objectives there is a need for the replacement or reshaping of tooth structure. The main challenges for years have been the development and selection of biocompatible, long lasting, direct filling tooth restoratives and indirectly processed prosthetic materials which can withstand the adverse conditions of the oral environment (Anusavice, 2003). Historically, a broad diversity of materials has been used as tooth crowns and root replacements. These have included human teeth, animal teeth, ivory seashells, bone, metals and ceramics. The use of restorative materials however for the replacement of missing parts of tooth structure has increased slowly over the centuries (Anusavice, 2003).

Dental materials may be applied as preventative restorations. The four categories of materials used in dentistry today are ceramics, metals, composites and polymers. Despite modern enhancements in the physical properties of these materials, none of these are permanent. Dentists and materials scientists will therefore continue explorations in the 21st century for the ideal restorative material. The ideal characterisation of a hypothetical restorative material should (1) be biocompatible (2) bond consistently to tooth structure or bone; (3) match the natural appearance of tooth structure and other perceivable tissues; (4) demonstrate properties similar to those of tooth enamel, dentin, and other tissues; and (5) be able to initiate tissue repair or regeneration of missing or damaged tissues (Anusavice, 2003).

The fundamentals for aesthetic and functional restorations have been simplified by the evolvement of resin based composites. The potential for greater application of resins came about with the launch of dental resin, bisphenol-A glycidyl methacrylate (Bis-GMA) (Leinfelder, 1997). Since its introduction, various other dental resins have also been developed, to overcome the problems of shrinkage, wear resistance and low strength. Furthermore, inorganic filler size has been a crucial area that can be controlled to improve these properties. The first generation of composites were not applicable to posterior restorations due to poor wear resistance and rough surfaces (Leinfelder, 1997). This was due to the large particle size of fillers used in this composite. In the 1970's, microfilled composites composed of silica with a particle size of about 0.04 μm were developed to improve wear resistance and produce a lustrous surface.

The mechanical properties of hybrid composites have recently been improved by incorporating glass particles (of different sizes) as fillers, for example, quartz SiO_2 , aluminosilicate (Al_2SiO_5) and silica glasses, to provide improvements in strength and a smooth surface (Yoonis & Kukletová, 2009).

A number of developments are still ongoing to provide dental materials of adequate clinical success (Edward & Swift, 2010). Continued investigations into decreasing the size of fillers to improve properties has recently led to the expansion of dental composites based on nanotechnology. Nanotechnology engineering is the manufacture of functional materials, with particle sizes in the range of 0.1 to 100 nm by different physical and chemical methods.

The newly available nanomaterials are incorporated throughout the resin matrix, whereas in nanohybrids the nanoparticles are combined with more traditional filler technology. The use of both can yield good composite materials, but the nanohybrid approach still might succumb to the loss of larger particles and the potential loss of early gloss (Edward & Swift, 2010).

Nanocomposite restorative materials exhibit the characteristics of being aesthetically appealing; they have high polishability and a very low degree of polymerisation shrinkage. The development of nanocomposite restorative materials that have improved aesthetic characteristics of high translucency and lustre, which still ensuring strength and wear resistance, now provides clinicians with a dependable option for anterior and posterior restorations (Mitra *et al.*, 2003).

Global recognition of the poor aesthetic value and potentially toxic effects of amalgam has resulted in the increasing replacement of the amalgams with dental composites. This replacement is done even in the posterior area of the oral environment, where amalgams normally exhibit more desirable wear characteristics than composites (Kahler *et al.*, 2006). Not only is the use of composites in restorations competing with the use of amalgams today, but there is also the potential for composites to completely replace amalgams for restorative materials (Roeters *et al.*, 2004). Used initially and mainly as small restorations, composite usage has increased to include indirect replacements for large cusp bearing restorations, crowns and bridges. In spite of the increased use of dental composites as restorations in large stress bearing areas and for amalgam inlay replacements, available data of properties, such as wear, flexibility and flexural strength are limited which is a cause for concern (Ferracane, 2006).

The long term mechanical properties of dental composites are generally investigated under simulated oral conditions. The intra-oral behaviour of restorative materials is a complex process in which masticatory loading in the presence of a chemically active environment accounts for degradation of the restoration. Over time, the deterioration is evaluated in general terms of wear, marginal breakdown and fatigue fracture due to cyclic loading (Braem

et al., 1994). Since the level of masticatory force, which impacts on a restoration surface, is time uneven, as well as the amount of chewing cycles per day, statistical investigations have been performed to determine cyclic loading circumstances. Braem *et al.* (1994) proposed average human chewing stresses to be between 5 MPa and 20 MPa at a chewing frequency of approximately 2Hz. Daily chewing performance is difficult to observe since chewing duration, chewing stresses, chewing cycles, food consistency or bilateral changes during mastication account for wide variations in data (Mioche *et al.*, 2002).

1.2 Problem statement

Wear resistance of dental composite continues to be of particular importance when restoring large occlusal areas in posterior teeth. Wear resistance of restorative composite materials is of cardinal clinical concern for restorations involving occlusion, because when the cusp tips of artificial teeth wear down and become flat it affects the chewing efficiency. The relatively poor wear resistance of dental composites in stress bearing posterior situations has restricted the wider clinical application of this type of restorative material.

Microfillers, due to particle size, are not very polishable. Hence they are rough and prone to the accumulation of plaque and stain. The relatively soft acrylic polymer tends to wear below the level of smoothness of the microparticles, which constantly separate from the composite surface, leaving voids.

1.2.1 Background to the problem statement

Historically, dental composite materials have not provided the wear resistance properties needed for posterior stress bearing areas (Gordan *et al.*, 2000; Yoshida *et al.*, 2001). Excessive force exerted on the dental composite material over time produces fatigue related to the amount of wear (Callaghan *et al.*, 2006). Whitters *et al.* (1999) found that the main improvements required on resin composites were in the areas of polymerization shrinkage and insufficient wear resistance under high masticatory forces.

Although initially applied extensively in the anterior region where there is a lower bite force is, composites were also used, with limited success, for posterior restorations (Yoshida *et al.*, 2001). Even with improvements and developments in composites, in term of properties such as elastic modulus, strength or resistance to fatigue, the wear resistance of dental composite materials is still taking place. it has been difficult to determine whether the ideal wear resistant characteristics for these materials (Ferracane, 2006; Gordan *et al.*, 2000; Yoshida *et al.*, 2001; Callaghan *et al.*, 2006; Rueggeberg, 2002; Bohlsen & Kern, 2003; Heintze *et al.*, 2005).

In the past, some manufacturers of dental composites promoted their products on the basis of it being the ideal wear resistant material for posterior restorations (Le Roux, 2008). However, the ideal composite material to resist wear for large stress bearing posterior restorations still needed to be developed (Ferracane, 2006; Gordan *et al.*, 2000; Yoshida *et al.*, 2001; Oh *et al.*, 2002). Ferracane (2006) indicated that although wear of small restorations is of insignificant clinically, the wear of dentals for large stress bearing restorations still has to be investigated. Additional improvements of flexural and fracture strength are therefore required to assure performance and longevity of cusp replacing resin composite restorations (Fennis *et al.*, 2005).

Wear may be attributed to direct opposing tooth contact during bruxism, which is termed "two body wear", or indirect contact through trapped food particles during the closed phase of mastication and termed "three body wear" (Potts *et al.*, 2004). To prevent these problems, the wear resistance of artificial restorations needs to be equal in strength to that of a natural tooth, particularly since the biting force derived from artificial teeth is greatly reduced (Hardy, 2001). If the cusp tips of artificial teeth wear down and become flat the biting force is reduced to the extent that the chewing efficiency is ineffective, and only soft foods can be taken. Careful selection of restorative materials and the need to introduce improved materials with regard to wear resistant properties needed therefore to be investigated (Oh *et al.*, 2002).

1.3 Research hypotheses

Incorporation of filler particles into a resin matrix for dental composites greatly improves the materials properties, provided that the filler particles are well bonded to the matrix; if not, the filler particles do not provide reinforcement and can actually weaken the material.

Decreasing the size and the agglomeration of filler nanoparticles is the key to improving the wear resistance of nanocomposites materials.

1.4 Aims and objectives

The principal objective of this study was to increase wear resistance while maintaining adequate flexural strength and surface hardness in dental composite restorations by designing and formulating TiO₂ nanocomposite materials that incorporating nanoparticles and a silane with the resin matrix.

1.4.1 Specific objectives

1. To introduce a silane bond between the nano-TiO₂ particles and the resin matrix to reduce the agglomeration of the TiO₂, and then to determine the effect of the

concentration of the silane coupling agent 3-(methacryloyloxy)propyltrimethoxysilane (MPTMS) on wear resistance, flexural strength and surface hardness of the nanocomposites.

2. To determine the effect of the nano-TiO₂ size on the nanocomposites materials in order to establish which size of nano-TiO₂ particles afford a nanocomposite with the most desirable design, wear resistance, flexural strength and surface hardness.
3. To investigate the effect of adding a small amount of nano-TiO₂ particles to the control sample (SR Adoro®).

CHAPTER TWO

LITERATURE REVIEW

2.1 Historical overview of dental materials

Dentistry has unique discrimination for the use of the widest diversity of biomaterials. Biomaterials can be divided into two main classes: natural and synthetic biomaterials (Ratner *et al.*, 2004). Natural biomaterials are extracted from animal and plant tissue. These materials are useful in the field of biomimetic and are used for implants corresponding and familiar to the body tissues. These materials also do not pose problems of toxicity often faced by manufactured materials (Oliveira & Reis, 2011). Furthermore, they may carry particular protein binding sites and other biochemical signals that may help in tissue healing or integration, for example, collagen used for bones, tendons, ligaments and skin. In such a case, it is implanted in a sponge that does not have relevant mechanical strength or stiffness (ASMI, 2003). Other natural biomaterials are: corals, chitin that can be extracted from different sources such as insects and crustaceans, keratin which is derived from hair and cellulose isolated from plants. Natural biomaterials however can be exposed to problems of immunogenicity. In addition, some natural polymers tend to denature or decompose at temperatures below their melting points. This severely limits their fabrication into implants of different sizes and shapes (ASMI, 2003).

2.1.1 Ceramics

Ceramic materials are either synthetic or natural materials that can be applied to dentistry and have the capability to mimic natural teeth. All ceramics metal oxides have corresponding compositions. The principal components of dental ceramics and porcelain are quartz, feldspar and kaolin. Another significant component of porcelain is leucite. Leucite is a crystalline potassium aluminium silica mineral that is formed when feldspar and glass are dissolved within the porcelain. Leucite is generally added as a component because it reinforces, toughens, and raises the thermal expansion coefficient of normal feldspar porcelain. In addition to this, glass modifier and pigments (metallic oxides) are supplemented to porcelain for colour (Ferracane, 2001).

Since 1996 these materials have been used to manufacture inlays, veneers, and crowns, as facings on metal substrates, and even as dental bridges, which can be made completely from high strength ceramics (Abudalazez, 2008). Ceramic restorations are extensively made by building up the accurate aesthetic combinations of prefired, pigmented particles, and then refiring under vacuum to sinter them together and eliminate voids (Abudalazez, 2008). Voids are undesirable in biomaterials especially those to be applied in dentistry. Acidic bacteria can be accumulated in the voids and though acidic reactions the ceramics may dissolve,

rendering the biomaterials structure unstable. Porcelain is a particular type of ceramic that has been used extensively in dentistry. The first dental use of porcelain was for denture teeth, and later, porcelain crowns called "porcelain jacket crowns" were developed for restoring anterior teeth that bore little or no occlusion. Ceramics are generally very brittle materials, and thus they cannot be twisted or deformed to any scope without actually cracking and breaking. They are produced by fusing oxide powders together in high temperature furnaces. Most pigments used in dentistry are metallic oxides. Their inclusion in suitable ratios enables the ceramist to produce nearly any colour conceivable. This characteristic also provides the dentist with the ability to match almost any tooth colour with aesthetic outcomes that are unattainable with other materials (Ferracane, 2001).

Porcelain is fundamentally made from white clay, quartz and feldspar. The components are pulverised, mixed, formed into shape and baked (Kelly *et al.*, 1996).

Three sorts of porcelains are common in dentistry. One particular type is used to construct denture teeth. This porcelain is called "high fusing" because it fuses at approximately 1300 °C to 1350 °C. A second type of porcelain is known as low fusing porcelain and has a fusion range of 850 °C to 1050 °C and is used as a veneer for metal in Porcelain fused to metal (PFM) restorations. A medium fusing porcelain (fusing point of 1100 °C to 1250 °C) is used for the anterior porcelain jacket crown and has properties intermediate between those of the low and high porcelain types (Ferracane, 2001).

2.1.2 Metals

Metals are further class of synthetic biomaterials which have functional properties, including strength, toughness and malleability and are commonly used in medicine and dentistry in implantable or prosthetic materials. They are easy to fabricate into a usable form. Metals are stiff and resilient with high a modulus of elasticity and shear. An application of alloys and special fabrication method process provides a wide range of alternatives in selecting the best metals for a specific use (Ferracane, 2001). The metal alloys have received particular attention as dental and orthopedic implants since these materials are well received by the body, partially due to the comparatively nonreactive surfaces (Ratner *et al.*, 2004).

Metals are widely used as structural components for the restoration or replacement of tooth structure. In particular, they are used in the posterior region of the mouth where the metallic colour is not repulsive. Besides, they are used more conservatively to replace parts of a tooth. When the portion of the tooth to be replaced is within the cusps, it called an inlay. When one or more cusps are comprised in restoration, but the complete crown is not replaced, it is called onlays. In general, the remaining teeth used as supports for metallic bridges that span the empty spaces to fill in the arch. These bridges are permanently fixed on the teeth with dental cement. Due to the fact that they replace only a part of the dentition,

they are often called fixed partials (Ferracane, 2001). When a patient has lost several teeth, or when it is necessary to reproduce lost or defective gingival tissue with the dental prosthesis (often called a dental appliance), removable partial denture is essential. The metal clasps are an extension of the metal body or structural component of the removable partial denture, which supplies it with strength and stability.

Titanium and titanium alloys have been developed as dental casting alloys and they are used with porcelain. Titanium is greatly reactive with oxygen and has an extremely high melting point. Therefore, special casting apparatus is required in the fabrication of dental prostheses from titanium (McCracken, 1999). Although titanium has superior biocompatibility, the extra processing and cost required to cast this metal has restricted its use as a dental restorative material (Ferracane, 2001).

2.1.3 Polymers

Polymers are primarily organic substances that constitute a further class of synthetic biomaterials. They are large molecules comprised of repeating structural units, called monomers. Polymer materials can be divided into inorganic and organic types. See Table 2.1. Currently, synthetic polymers are used practically in nearly every industry and area of life. In dentistry polymers are extensively used as adhesives and lubricants, as well as structural components such as dentures (Allcock *et al.*, 2003).

Table 2.1: Classification of polymers
(Allcock *et al.*, 2003)

Inorganic		Organic	
Natural	<ul style="list-style-type: none"> ✓ Clays: bricks, cement, pottery ✓ Sands: glass 	Natural	<ul style="list-style-type: none"> ✓ Polysaccharides: adhesives, fibers ✓ Proteins: adhesives, fibers ✓ Polyisoprene: rubbers
Synthetic	<ul style="list-style-type: none"> ✓ Fibers 	Synthetic	<ul style="list-style-type: none"> ✓ Adhesives, fibers, coatings, plastics, rubbers

In dental work, polymers are used comprehensively as temporary restorative materials for single restoration and bridges to be worn while the imperishable metallic or ceramic restoration is being constructed in the laboratory. They are used as adhesive agent to improve the bonding between diverse materials and tooth structures or as sealants of pits and fissures present on the occlusal surfaces of permanent teeth (Ferracane, 2001).

2.1.4 Composites

Composites are compounds of two or more distinctly different materials with properties superior or intermediate to those of the distinctive components or constituents (Mars, 1998;

Shama, 2006). Dental composites offer virtually limitless possibilities for the development of replacement materials because it is characteristically superior to and lower in cost than dental ceramic and metal alloys (Ruddell *et al.*, 2002). Composites generally contain hard, pebble-like filler particles that are encircled a second material's hard matrix binding the filler particles together. The coarseness of the filler particles varies from sizeable rocks to microscopically fine powder of shapes varying from spherical fibres to flakes. The matrix material starts out as a paste or liquid that starts hardening when activated, either by adding a catalyst (which may be mixed with the filler particles), or by adding water or another solvent to facilitate chemical reactions. It can be pressed into a mold before it hardens. Bis-GMA quartz/silica filler and Poly(methylmethacrylate) PMMA-glass fillers are the most successful composite biomaterials used as restorative material or dental cements in dentistry today (Davis, 2003). The success is due to the filler particles being coated with a silane coupling agent that comprises a methacrylic group able to copolymerize with the matrix to ensure bonding between the filler and the matrix.

Of importance to composites are the properties and volume fraction of the respective phases, namely the continuous phase (the matrix) and the dispersed. Composites are generally classified based on the shape or nature of the dispersed phase, for example, particle reinforced, or fibre reinforced composites (Askeland & Fulay, 2003). Fillers are distinguished by particle size and distribution, geometry and surface area. Harper *et al.* (2000) illustrated that smaller particles achieve better properties enhancement compared to larger particles.

2.2 Optimisation of dental resin composites

Resin composites were introduced for dental restoration materials in the mid-1960s because of their exceptional characteristics such as mechanical properties, ease of preparation, aesthetic properties and biological compatibility (Karbhari & Strassler, 2007; Xia *et al.*, 2008). As a result, they are widely used as an alternative to conventional dental amalgam alloys. Resin composites compensate for the negative and undesirable aspects of amalgam alloys, such as toxicity, corrosion, pollution and colour (Clarkson *et al.*, 2003).

The indirect composite inlay technique was launched in Germany (Mormann, 1982) and in France (Touati, 1996). The technique provided the ease of fabrication, reduction in marginal shrinkage and efficiency in building the proximal contacts and contours. (Fruits *et al.*, 2006) showed that restoration with indirect resin was associated with less microleakage than the direct resin groups.

The SR Adoro® is an indirect composite introduced by Ivoclar Vivadent, (Schaan, Liechtenstein). It consists of large filler particles (about 1.5 µm) which are combined with

microfillers by copolymers (Le Roux, 2008). It does not contain Bis-GMA or triethylene glycol dimethacrylate (TEGDMA). It contains a urethane dimethacrylate (UDMA) which makes it less susceptible to water absorption and solubility (Le Roux, 2008). The large filler particles impart high filler loading resulting in high physical stability and low polymerization shrinkage. However, this also leads to high wear and tear followed by rough surfaces and thus leading to increased plaque accumulation. The microfillers are added to combat the disadvantages of the large filler particles (Zandinejad et al., 2006).

SR Adoro® is suitable for the fabrication of both metal supported and metal free restorations. Final polymerization tempering is performed in the light curing unit by means of light and heat (Zandinejad et al., 2006).

Lutz et al. (1984) showed ameliorations in wear resistance of a heat cured formulation over light cured and chemically cured formulations. Wendt (1987) reported an increase in the diametral tensile strength and hardness without a decrease in compressive strength and modulus when light cured composites were further subjected to heat treatment for 10 minutes at 100 °C to 200 °C. (Cook & Johansson, 1987) showed an increase in diametral tensile strength, flexural strength and fracture toughness of composites post cured at 100 °C for 24 hours.

Ferracane & Condon (1992) studied the fracture toughness, elastic modulus and surface hardness of composites after three different post curing light treatments. They reported an increase in fracture toughness and modulus of elasticity but the alterations in surface hardness were inconclusive. They also correlated the increase in the degree of conversion with the enhancement in the mechanical properties. In addition, they identified that relaxation of internal stresses at the filler matrix interface is another outcome of post cure heat treatment which may improve adherence between the resin matrix and fillers and improve the mechanical properties.

2.2.1 Dental resin matrix

Typically, dental resin composites mainly contain a resin matrix, various inorganic fillers and initiating agents. The structure of 2-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethoxy]ethyl 2-methylprop-2-enoate, commonly known as triethyleneglycol dimethacrylate (TEGDMA) , is shown in Figure 2.1.

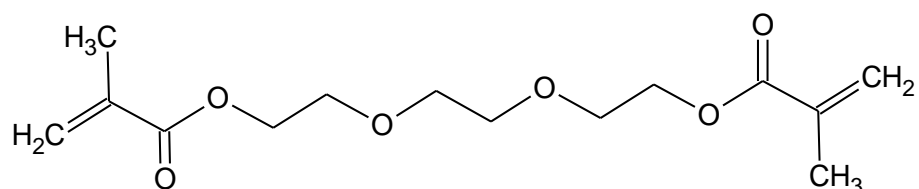


Figure 2.1: Structure of 2-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethoxy]ethyl 2-methylprop-2-enoate commonly known as triethyleneglycol dimethacrylate (TEGDMA)

TEGDMA is added as a diluent to ([2-hydroxy-3-[4-[2-[4-[2-hydroxy-3-(2-methyl prop-2-enoyloxy) propoxy] phenyl] propan-2-yl]phenoxy] propyl] 2-methylprop-2-enoate) (Bis-GMA), which is shown in Figure 2.2 and is the most common monomer in resin composites (Atai *et al.*, 2005; Sideridou & Achilias, 2005). Due to the high viscosity of Bis-GMA (up to 1200 Pa.s), it remains a challenge to add inorganic particles into the resin matrix. Without the inorganic fillers, the dental resin composites tend to generate high polymerization shrinkage during the curing stage and low mechanical properties, which can lead to secondary caries. It is therefore important to devise ways of introducing inorganic fillers into resin composites (Wang *et al.*, 2011).

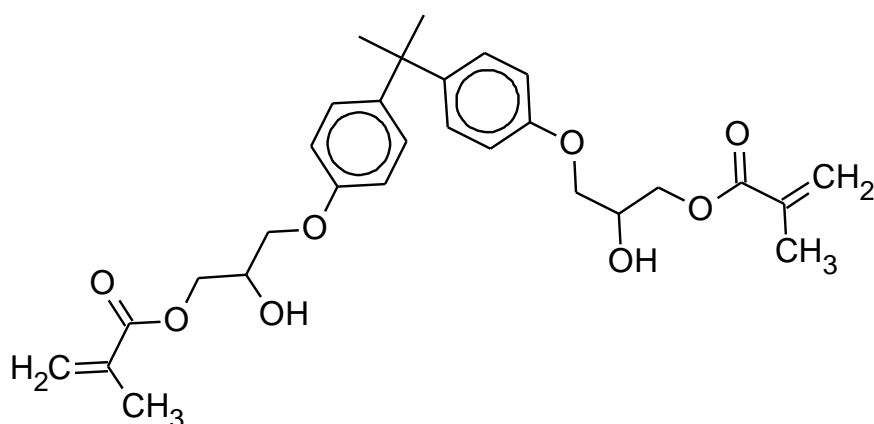


Figure 2.2: Structure of bisphenol a glycidyl methacrylate ([2-hydroxy-3-[4-[2-[4-[2-hydroxy-3-(2-methyl prop-2-enoyloxy) propoxy] phenyl] propan-2-yl]phenoxy] propyl] 2-methylprop-2-enoate) (Bis-GMA)

Many commercially available dental resin composite materials, at present, use Bis-GMA, a major monomer matrix. It is a viscous, bulky bifunctional monomer with high reactivity and molecular weight. Whilst undergoing low polymerization shrinkage, it produces a cross linked, three dimensional resin network (Peutzfeldt, 1997). Because of the high viscosity of Bis-GMA, the resin phase of dental composites has to be diluted to enhance the handling of composite pastes. TEGDMA is the resin matrix mostly used for this purpose. Diluting the

composite with TEGDMA has been shown to have less desirable effects on the properties of the resin, because it increases water absorption and polymerization shrinkage (Kalachandra *et al.*, 1993). On the other hand, lower polymerization shrinkage stresses may result from the relative ease of flow of diluted resin composites during the early stages.

Since 1965, most research and development of dental composite materials have only been conducted with short chain polymers such as urethane dimethacrylate, (2-[[3,5,5-trimethyl-6-[2-(2-methylprop-2-enoyloxy)ethoxycarbonylamino]hexyl]carbamoxyloxy]ethyl 2-methylprop-2-enoate) UDMA, which is shown in Figure 2.3 (Rueggeberg, 2002).

Shinohara *et al.* (2001) found that the concentration of base monomer is greatly influenced by a double bond conversion attained during polymerization as the isolated methacrylate carbon-carbon double bonds are converted to an extended network of single bonds, unreacted monomer fraction and cross linking.

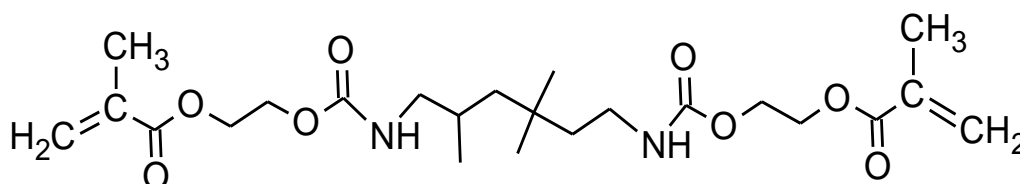


Figure 2.3: Structure of urethane dimethacrylate, (2-[[3,5,5-trimethyl-6-[2-(2-methylprop-2-enoyloxy)ethoxycarbonylamino]hexyl]carbamoxyloxy]ethyl 2-methylprop-2-enoate) (UDMA)

2.2.2 Fillers

Fillers' effect on the mechanical properties (bulk and marginal fracture, strength degradation, cyclic fatigue, wear resistance) and physical properties (shrinkage, shrinkage stress/strain, colour stability) of restorative composites has been extensively investigated (Braga *et al.*, 2005). The influence of the methacrylate resin matrix, filler type and filler loading on material properties have been widely reported (Simone & Norbert, 2005). Still, the properties of individual inorganic fillers incorporated in the organic matrix are not fully understood. Characterisation of fillers in modern restorative composites is complex because there are many different filler types, morphologies and size distributions. (Beun *et al.*, 2007).

The type of fillers considerably influences the properties of composite restoratives. The composite restoratives are classified according to the type of fillers used (Lutz *et al.*, 1983). This classification, despite being nearly twenty years old, is still valid for modern dental composite materials. At present, macrofilled composites with an average particle size varying between 5 μm to 30 μm are less frequently used due to poor aesthetics. The fillers used are

characterised by different analytical techniques, the average particle size, and the chemical composition.

According to Nirschl (2003), an extremely small nanoparticle provides high opacity in unpigmented dental composites, which allows investigators to prepare a spacious variety of shades and opacities of dental composites and thus provide highly aesthetic restorations. In addition spherically shaped nanoparticles provide superior polishability (Rüttermann *et al.*, 2008).

As the monomer systems do not change much from case to case, composite restoratives has been commonly classified according to the types of filler added (Lutz *et al.*, 1983). Macro fillers are larger ground quartz or glass particles. The filler particles that were used in the first dental composites had diameters ranging from 20 to 40 μm and mainly consist of quartz (Darvell, 2002). Because it is so hard, quartz is difficult to grind into fine particles. These macro filled composites are resultantly used less frequently because of aesthetic concerns and the difficulty of achieving a smooth surface. Recent composites contain ground particles that are in the range of micron particle size or even smaller, such as pyrogenic silica.

Inorganic particles of nanometer size, such as silica, SiO_2 , (Kim *et al.*, 2007; Leprince *et al.*, 2010), tantalum, Ta_2O_5 , (Schulz *et al.*, 2008), titania, TiO_2 , (Schulz *et al.*, 2008; Khaled *et al.*, 2007) and zirconia ZrO_2 (Amirouche *et al.*, 2009) have been introduced into the synthesis of inorganic-polymer composite materials in the last five years. Due to their ideal mechanical properties such as flexural strength, hardness, low abrasion and high radiopacity, nanomaterials are extensively used for reinforcement in dental resin composites (Wang *et al.*, 2011).

In modern dental composites, the current trend to reduce filler size whilst aiming to improve the filler loading, seeks to optimise the resultant mechano-physical properties and clinical performance (Ferracane, 1995). The introduction of so-called nanofilled and nanohybrid materials, therefore, appears to be a logical continuation of this trend. A number of dental material manufacturers have marketed these composites as the advancement of dental materials into the field of nanotechnology (Mitra *et al.*, 2003). A nanomaterial possesses components and/or structural features, such as fibres or particles, with at least one dimension in the range of 1 to 100 nm and subsequently demonstrates novel and distinct properties (Liu & Webster, 2007). Researchers and manufacturers are still debating and speculating whether nano dental composites exhibit improved mechano-physical properties compared to existing dental composites (Curtis *et al.*, 2008). "Nano" is not a recognised classification. It is interesting to note that, despite the hype and extensive marketing campaigns by manufacturers, there is little difference in the particle size between the fillers of nano and the fillers of nanohybrid dental composites (Curtis *et al.*, 2008). Figure 2.4 shows a

diagrammatic illustration of the progress of dental composites employed by restorative dentistry and classified according to the size of the filler particles.

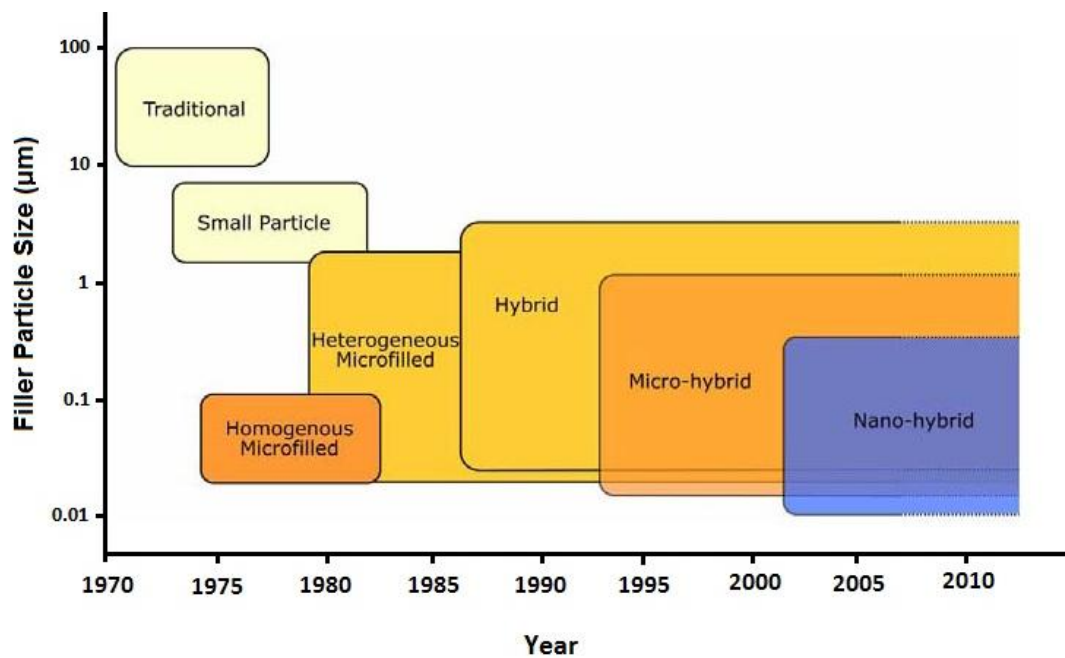


Figure 2.4: Diagrammatic representation of the development of dental composites (Curtis *et al.*, 2008)

Nanohybrid dental composites contain a mixture of colloidal silica particles with a size distribution of 20 to 60 nm and micron sized filler particles of 0.1 to 2.5 µm, such as borosilicate admixed with a methacrylate-based resin matrix (Curtis *et al.*, 2008). A novel substitute approach to the clinical application of nanofill technology in dental restorative materials has been a dental composite comprising a mixture of individually scattered filler particles of 5 to 75 nm and agglomerated nanosized particles of 1.3 µm, delineated as nanoclusters.

Beun *et al.* (2007) conducted an extensive investigation comparing the flexural strength, elastic modulus and Vickers' micro hardness of several nanofillers with general and micro filler dental composites materials. The study determined that the nanofillers, Filtek™ Supreme (3M ESPE) and Grandio™ (Voco), exhibit exceptional flexural strengths, surface hardness values and elastic modulus compared to the other dental composites materials tested, with the exception of Filtek™ Z100 (3M ESPE). Subsequently, both nanofiller materials were advisable for posterior and anterior placement (Beun *et al.*, 2007).

The addition of even small amounts of nanosized silica particles has been recognised to improve the mechanical properties. Tian *et al.* (2008) indicated that the addition of 1 to 2.5 wt

% of nanosized fibrillar silica to a Bis-GMA/TEGDMA resin significantly improved the flexural strengths (128 and 130 MPa) compared with conventionally dental composites materials, (110 and 120 MPa respectively). This was thought to occur as a result of the reinforcing effect of highly separated and uniformly distributed nanofibrillar silica, whilst the formation of agglomerates of fibrillar silica may debilitate the resulting material (Tian *et al.*, 2008).

The wear resistance of the composites in the oral cavity depends on the space available between filler particles providing protection against food bolus. The presence of smaller filler particles reduces inter-particle spacing in the composite, improving its wear resistance (Bayne *et al.*, 1992).

More studies into the application of particles in nanosize range as fillers in polymeric composites are conducted. The presence of nanoparticles ameliorates mechanical properties of the materials, due to their high specific surface area to volume ratio. The use of nanoparticles can give the material with better characteristics, due to interfacial interactions, resulting in remarkable properties (Laine *et al.*, 2001; Wetzel *et al.*, 2002).

Nanoparticles exhibit a more homogeneous filler distribution in low viscosity materials, such as bonding agents, which restricts 'filler settled', namely filler-rich, regions within the matrix (Wilson *et al.*, 2005). The incorporation of nanosized filler in bonding agents also produced a more homogeneous bond to the tooth/bonding agent interface as filler penetrates the dentine tubules to reinforce the hybrid zone (Breschi *et al.*, 2008).

Another phenomenon contributing to the aesthetic appearance of nanofilled composite materials is that such materials appear translucent as a result of the small size of the homogeneously distributed nanosized filler particles. This occurs as the particle size is smaller than the wavelength of incident light (400 to 700 nm), the resultant scattering coefficient is decreased allowing light to pass through the composite materials without deflection at the interface between the resin matrix and inclusions, such as filler particles and porosity voids (Lee, 2007).

Nanofillers are filler particles smaller than 100 nm. Pyrogenic or fumed silica fillers are regularly used as filler materials in dental resin composites. It is difficult to achieve high filler loading using only nanofillers (because of the excessively large surface area), and hybrid composites, comprising a mixture of microsize (about 1 μm diameter) and nanosize, are therefore normally used. As a result of the higher filler loading, such mixed composites provide a relatively smooth surface and better mechanical properties (Anusavice, 2003).

One of the most important characteristics of nanoparticles is its very large surface area, causing a very strong thickening effect. In other words, the viscosity of the paste of such composites is much higher than those filled with larger particles at the same filling level

(Darvell, 2006). The volume fraction of filler needs to be decreased in order for dentists to prepare a workable paste. It can, however, be expected that the elastic modulus and strength would be decreased and the shrinkage would be increased, raising the defect rate or making it unsuitable for posterior restorations. It is also expected that there would be a higher degree of agglomeration between nanosize particles (Darvell, 2006).

2.2.2.1 Nano titanium dioxide (TiO₂)

There is significant interest in TiO₂ because it has so many potential applications, for example as chemical sensors, as a glass coating material for antifogging and self-cleaning, and as a biomedical material. TiO₂ is also cost effective and chemically stable, with good optical properties, thermal stability, high refractive index, and a deficiency of absorbance of visible light. A number of studies have shown that TiO₂ can act as a bioactive material by offering strong interfacial bonding to living tissue (Roether *et al.*, 2002; El Fray & Boccaccini, 2005).

Using nano-TiO₂ particles as fillers in epoxy, some researchers have found that its presence can overcome the drawbacks of traditional tougheners, like glass and rubber beads by improving the stiffness, strength and toughness of the epoxy without sacrificing its thermo-mechanical properties (Li *et al.*, 2011). Nano-TiO₂ particles are very fine and agglomerate easily in practical applications. They are particularly difficult to disperse in organic solvent (Young *et al.*, 1998). Some surface treatment of the nano-TiO₂ particles is required to overcome this problem. Inorganic fillers in dental composites are normally treated with organo silane in order to improve the bond strength to the resin matrix and increase the service life of the composite (Zheng & Zhou, 2007). An additional benefit of using this substance is the improved homogeneous dispersion of silanated filler particles throughout the matrix.

2.2.2.2 Silicon dioxide (SiO₂)

SiO₂ is a crystalline metal occurring profusely as sand, quartz and many other minerals and is used to produce a diversity of materials, particularly concrete and glass. Natural silica is nonreinforcing and has been used as a filler, only to reduce the cost. The synthetic ones reinforce and nowadays have particle sizes as small as the carbon black besides a highly reactive surface (Kohjiya & Ikeda, 2000). Important natural varieties are silica (crystalline), silica (microcrystalline) and silica diatomaceous (fossil origin). Types of synthetic silica are pyrogenic, precipitated, hydrogels and aerogels. Of this diversity, precipitated silica and pyrogenic (fumed) silica are being used for elastomer reinforcement (Kohjiya & Ikeda, 2000).

The reaction products are satisfied directly after coming out of the burner. Pyrogenic silica is too expensive (Kohjiya & Ikeda, 2000). Precipitated silica is silicon dioxide, including about 10 to 14% water, with particle size in the range of 1 to 40 nm. They are reinforcing fillers

giving composites tear resistance, high tensile strength, hardness and abrasion resistance and are used in the manufacture of translucent, coloured products and other mechanical rubber goods. Pyrogenic or Fumed silica is silicon dioxide containing less than 2% integrated water. These silicas are highly reinforcing fillers of very small particle size, giving tear resistance, good tensile strength and abrasion resistance especially to silicone rubbers (Maya, 2007).

2.2.3 Coupling agent

Silanes are a subclass of coupling agent that also includes titanites and phosphonates. Composite strength and toughness are decreased because the filler particles exhibit inconsistencies. Stresses are transmitted through the filler particles prominent from the occlusal surfaces through the boluses of foods during chewing. The inorganic filler particles are significantly stronger than the dental resin matrixes and the stresses are therefore transmitted through the filler to the resin (Fong, 2004). Only when effective bonding has occurred between the reinforcement and the matrix, does the relocation of stress between them occur. The procedures for using coupling agents in dentistry have been well developed (Le Roux, 2008). The surfaces of fillers are generally treated with methacrylate-functionalised silanes, such as the frequently used a MPTMS as shown in Figure 2.5, to produce covalent links between the inorganic filler particles and the organic resin matrix by free radical copolymerisation.

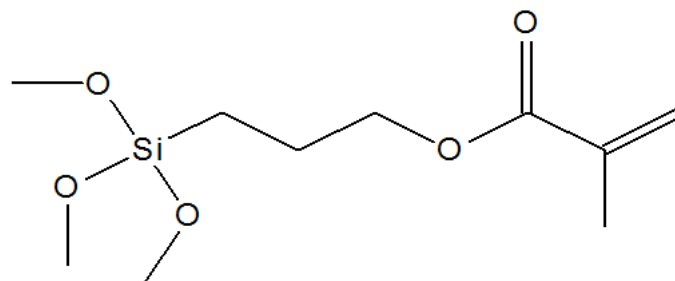


Figure 2.5: Structure of 3-(methacryloyloxy)propyltrimethoxysilane (MPTMS)

The silane adhesive bonding agent ensures success in dental composites. There is ample evidence indicating that fillers weaken the composite material in the absence of an adhesive silane bonding agent (Zandinejad *et al.*, 2006). The particles would act as stress concentrators and cause the different types of material to segregate (Anusavice, 2003).

Filler particles must be chemically bonded to the matrix because if they are not bound they detach from the matrix under tension strength. As a result, the filler does little to improve

properties of the composites (Davis, 2003). It also reduces the overall strength and toughness of composites because the filler particles act more like inconsistencies in the composites. Stress is only transferred between the reinforcement and the matrix when effective bonding has occurred between them. Figure 2.6 (a) and (b) show scanning electron microscopy (SEM) images of filler particles with and without good bonding in the dental composites, respectively.

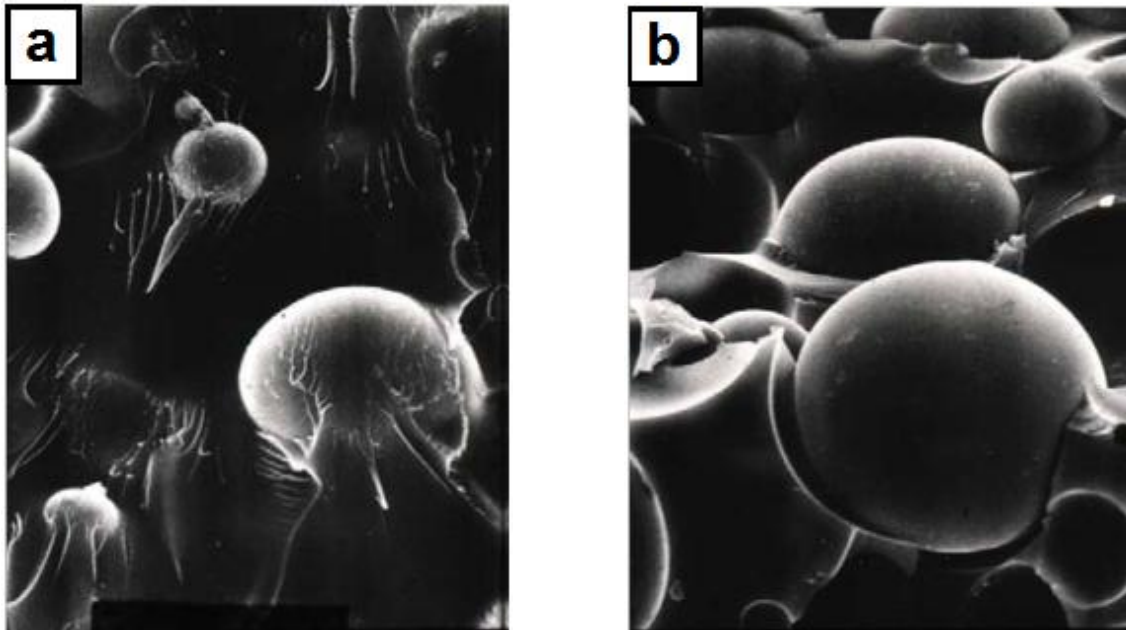


Figure 2.6: SEM images of (a) filler bonded to matrix and (b) filler not bonded to matrix (Davis, 2003)

This type of bonding between filler and matrix is much stronger than any other potential bonds, such as hydrogen bonding or Van der Waals forces. For particles other than silica, (which contain surface hydroxyl groups), similar silanising agents are also used. Ash *et al.* (2004) show that a strong bonding between alumina and PMMA can productively influence the thermal behaviour of alumina/PMMA nanocomposites, characterized by an alteration in the glass transition temperature (Somasundaran *et al.*, 1999; Ash *et al.*, 2004).

In composites there is a phase known as the interfacial region, which begins at the point in the filler at which the properties differ from those of the bulk filler and ends at the point in the matrix at which the properties become identical to those of the bulk matrix (Drzal *et al.*, 1985). Although this is a small region in conventional composites, it is crucial in controlling the properties, i.e. the chemistry of bonding, polymer chain mobility, degree of conversion, and crystallinity. This region can extend up to 2 to 9 nm in thickness around the particles (Hergeth *et al.*, 1989).

Multifunctional urethane and thioether(methacrylate)alkoxysilanes have been developed as dental restorative bonding materials for the synthesis of inorganic–organic copolymer composites with filler particles in the nanometer range. The methacrylate groups are available for photochemically induced organic polymerization while the alkoxysilyl groups of the silane allow the formation of an inorganic Si-O-Si network Figure 2.7 by hydrolysis and polycondensation reactions (Anusavice, 2003; Papadogiannis et al., 2007). Understanding of silane bonding mechanism for bonding resins to non etchable filler material such as zirconia and alumina is, however, restricted and additional tests involving silane bonding with these materials, as well as efforts to enhance these bonding mechanisms, are required (Matinlinna *et al.*, 2004).

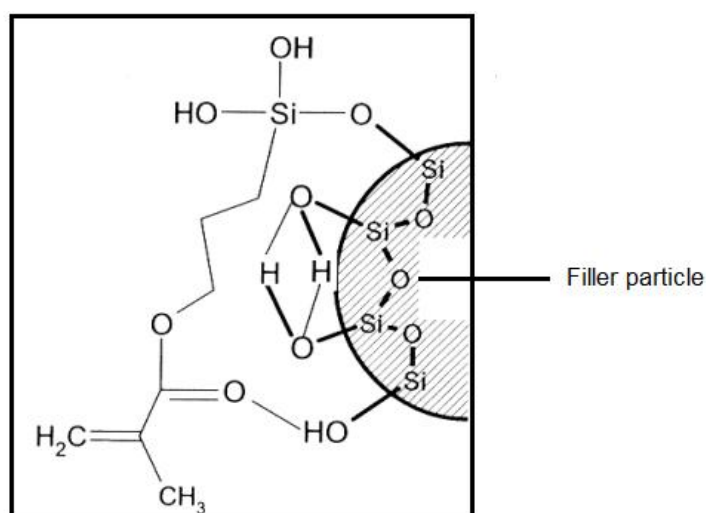


Figure 2.7: Illustration of chemical bonding of MPTMS silane with Si-O-Si network (Anusavice, 2003)

The constructional characteristics of coupling agents on particle fillers are determined by on a number of variables, with the concentration of the coupling agent having a considerable effect. In dilute solution, γ -MPS has been shown to adsorb on clay and lead oxide particles in monomolecular layers (Miller & Ishida, 1984). The arrangement of γ -MPS on the substrates was shown to be parallel to the surface with a specific surface area per molecule of 0.60 and 0.59 nm² on clay and lead oxide, respectively. This coverage compared favorably to space filling projections for γ -MPS in a parallel orientation relative to the surface (0.55 nm²). On colloidal silica, estimates of 0.43 to 1.04 nm² per molecule have been reported (Soderholm & Shang, 1993). Adsorption of γ -MPS in an equidistant orientation approaching a monomolecular coverage, however, is not necessarily suitable for optimum reactivity with the resin matrix, or for physical mechanical reasons. For these reasons, silanes are often processed at concentrations that yield structures that deviate considerably from the ideal molecular packing obtained from dilute solution. Disturbances in the molecular arrangement

at the surface occur at increased concentration through association between silanols resulting in adsorption of higher molecular weight species (Ishida & Koenig, 1979). Studies with γ -aminopropyltriethoxysilane (γ -APS) and epoxy resin have shown that their reactivity with each other is dependent upon the extent of condensation of the silane interphase (Culler *et al.*, 1986). This result is due to reduced diffusion of resin into the polysiloxane network at increased condensation (Culler *et al.*, 1986).

The chemical similarity between the silane methacrylate functional group and that of the matrix methacrylates yields a virtually indistinguishable infrared signature. It is possible that this similarity will complicate the analysis of the degree of matrix polymerisation of the based silane methacrylate is present at detectable concentrations and structural variables (for example, steric limitations) within the interphase leave methacrylate unreacted silane. Such conditions would lead to underestimation the actual resin matrix conversion when considered in the conventional manner. Preliminary investigation by the authors proposed that the silane content on the filler could provide a measurable reduction in the conversion for model resin based composites and that most of the silane $-C=C-$ bonds presented would be unreacted (Halvorson *et al.*, 2003).

2.3 Analytical chemical characterization techniques

The limit of conversion of dental polymers based on methacrylate resins has been characterised by a number of chemical analytical methods. These are nuclear magnetic resonance spectroscopy (NMR) (Lloyd *et al.*, 1994; Heatley *et al.*, 1995), differential scanning calorimetry (DSC) (Abadie & Appelt, 1989), raman spectroscopy (RS) (Shin *et al.*, 1993), scanning electron microscopy (SEM), transmission electron microscopy (TEM) (Brandon & Kaplan, 2008) and fourier transform infrared spectroscopy (FTIR) (Rueggeberg *et al.*, 1990).

2.3.1 Fourier transforms infrared spectroscopy (FTIR)

FTIR spectroscopy was used extensively due, in large part, to the availability of apparatus and numerous sampling techniques. The vibration ally mode typically analysed in infrared examination of methacrylate-based dental materials involves stretching of the carbon-carbon absorption bond of the methacrylate moiety concentrated on around 1638 cm^{-1} (Shin *et al.*, 1993). Dissimilar monomer reactivities may account, in part, for differences noted among materials within a given study (Lovell *et al.*, 1999). Comparison of conversion values across studies may show additional deviations due to differences in the baseline parameters used to define the pertinent absorption bands needed to quantify conversion (Rueggeberg *et al.*, 1990). The term conversion, for resin-based composite, generally refers to the percentage of $-C=C-$ bonds of the matrix monomers which have reacted. Additional $-C=C-$ bonds on, for

example, silane molecules can lead to errors in determining the conversion. The magnitude of such an error is expected to be related to the amount and reactivity of the silane on the filler. Silane coupling agents are used to promote adhesion between filler and matrix polymer and also to increase the hydrolytic stability (Bowen, 1963). In dental resin-based composite materials, the organofunctional silane, γ -(methacryloxy)propyltrimethoxysilane (γ -MPS), has been used extensively (Bowen, 1963). The enhanced stability of composites compounded with filler treated with γ -MPS or with other silane coupling agents, is attributed, in part, to the formation of a siloxane bond between the filler and the coupling agent (Ishida & Koenig, 1979). Additionally, covalent bonding may occur between the organofunctional group of the silane and reactive groups of the resin matrix (Ishida & Koenig, 1979). The reactivity depends not only on the chemical nature of the reactants, but also on the spatial arrangement of silane on the filler.

2.3.2 Scanning electron microscopy (SEM)

SEM uses a focused electron beam to image the surface. The image is obtained by scanning the focused electron probe across the surface and collecting the resulting image signal from the surface. The signal is collected from the specimen surface and the electron beam loses energy by inelastic scattering as the electrons penetrate beneath the sample surface. Most of the electron current from an excited sample is due to the release of secondary electrons from the sample surface (Brandon & Kaplan, 2008). Changes in the local curvature will change the probability that a secondary electron can escape. A region with a positive radius of curvature increases the chances of the secondary electron to escape and vice versa, while the regions with negative radius of curvature reduces the secondary electron current. Since the intensity of the image depends upon the number of secondary electrons reaching the detector, secondary electron imaging provides topographic images of rough surfaces (Brandon & Kaplan, 2008).

2.3.3 Transmission electron microscopy (TEM)

TEM uses a focused electron beam, the same way as the SEM. Both SEM and TEM require vacuum conditions to operate. In TEM the detector is however detecting electrons transmitted through the sample. This sets limitations on the specimen thickness, which should be less than 0.1 μm to allow most of the high energy electrons to pass without serious energy loss. This setup gives high resolution in two dimensions. The high energy electron beam has limited path length in air as the whole microscope column should be kept under a vacuum at 10^{-6} Torr and for the highest resolution, 10^{-7} Torr, is desirable (Brandon & Kaplan, 2008).

2.4 Analytical techniques for mechanical properties

2.4.1 Wear resistance of dental composites

The processes involved in composite wear are complex and poorly understood; there are two methods used to analyse wear behaviour of dental composites: *in vivo* and *in vitro* methods. The *in vitro* methods are used more often since it take less time, are simpler, more effective and of lower cost. But there is no test standard for the wear process. Among the published studies, large differences can be observed on the wear simulating devices, contact conditions, counter face materials and abrasive agents (Zheng & Zhou, 2007). Concerning the type of wear test geometry, ball-on-flat and pin-on-disk geometries are the most commonly used (Zheng & Zhou, 2007). The schematic view of the pin-on-disk wear tester is shown in Figure 2.8.

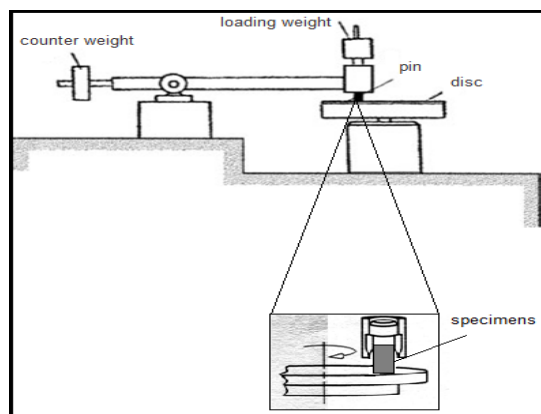


Figure 2.8: Schematic view of the pin-on-disk wear tester (Tagtekin *et al.*, 2004)

According to an investigation by Stina & Philip (2003), SR Adoro® has high wear resistance, and the importance of choosing a composite with high wear resistance is considered because of relatively high acceptable wear rates, ease of use for most dental composites and its compliance with the American Dental Association (ADA) requirements (Van Nieuwenhuysen *et al.*, 2003).

Dental composite materials have been stated to provide acceptable wear resistance in posterior stress bearing areas for small to moderate sized restorations (Ferracane, 2006). Evaluation of composite resin fillings and inlays in a study over eleven years suggests that dental composite materials are considered as a significant concern only when the patient has abnormal occlusal habits, such as clenching and bruxing (Ferracane, 2006). These studies do not consider the importance of striving to meet optimum requirements for wear resistance

of proven restorative materials such as gold and amalgam and suggest that inferior limits are acceptable (Van Nieuwenhuysen *et al.*, 2003).

2.4.2 Flexural strength of dental composites

Flexural strength is one of the most significant properties of restorative dental materials (Scherrer *et al.*, 2003) in correlation to the liability of fracture of restorations under occlusal load (Asmussen & Peutzfeldt, 2003). Chipping and bulk fractures are major causes of clinical failure of composite restorations. Failure is most likely to proceed by a slow subcritical propagation of internal flaws (Loughran *et al.*, 2005). Fatigue fractures of composites in clinical use were found to be a common reason for time related failure with frequent reports of damage to bulk, cusp, or marginal fractures of restorations (Lohbauer *et al.*, 2003). Cyclic fatigue of dental composites might result in individual loading cycles well below the ultimate strength of the material. The cumulative effects of cyclic loading results in crack formation and propagation that lead to fracture. Bulk fatigue characteristics of composites, are most commonly evaluated by subjecting the material to three or four point flexural loading (Al-Turki *et al.*, 2007).

Marquis *et al.* (2000) indicted that the influence of loading is predicted to be significant since occlusal function results in flexural, as well as, cyclic loading. Al-Turki *et al.* (2007) determined significantly lower flexural strength for specimens that were flexing loaded as opposed to contact loaded specimens. For the flexural loaded specimens, the aging, load, and the media were all significant while the number of cycles had no significant influence. For the contact loaded specimens the media, aging, and cycles completed, had a significant effect, but no effect was ascertained for the different cycling loads.

Al-Turki *et al.* (2007) concluded that the decrease in flexural strength from flex loading was principally affected by the aging media, whereas, the reduction from contact loading was accredited mainly to the number of cycles.

Flexural strength is increased by the incorporation of ceramic fillers. Stronger and more permeable fillers provide higher flexural strength (Zandinejad *et al.*, 2006). Much information concerning functional performance and design considerations of composite materials, for large restorations, is still lacking. Even with whiskers that significantly improve the properties of dental composites the use of composites in large stress bearing applications such as direct posterior restorations involving cusps, indirect crown and multiple unit restorations is not advised without risk (Xu *et al.*, 2003).

According to Walker *et al.* (2006) the flexural strength (S) can be calculated using the following equations:

$$S = \frac{f_{max} \cdot i}{b \cdot h^2}$$

Where

f_{max} = maximum load before fracture

i = distance between supports

b = width of specimen

h = height of specimen

The relatively high brittleness and low fracture resistance of modern composites still complicate their use for large stress bearing restorations (Xu *et al.*, 2003). Dyer *et al.* (2005) identified fiber reinforced composite, (FRC), but as substitutes for metal ceramic and all ceramic crowns and bridges, Fleming *et al.* (2005) noted that it has not yet been proven to be successful with long term clinical experiments. One of the causes for decreased confidence in the use of FRC material is an absence of information regarding the influence of design parameters on the mechanical performance of a composite prosthesis. Design influence as a result of the flexibility of composites and associated marginal leakage due to the plasticity of resin should be studied more extensively (Mesquita *et al.*, 2006). The inflexibility of dental composite materials should be as high as possible in order to withstand compressive, flexural and shear stress (Anusavice, 2003). Marginal leakage that appears from flexural and shearing stresses is exacerbated as a result of wear that causes disfigurement to the bonded composite around the margins (Bonilla *et al.*, 2001). High inorganic filler content has been shown to present lower shrinkage and higher stiffness values (Braga *et al.*, 2005). Higher stiffness and flexural strength values avert the composite material from breaking and flexing around the margins. The affinity between polymerization shrinkage stress and marginal integrity has been established *in vitro* in class V restorations (Caries affecting gingival 1/3 of facial or lingual surfaces of anterior or posterior teeth) (Braga *et al.*, 2005).

Longevity of dental composite would be further reduced if this were in a cusp condensed occlusal zone of marginal leakage. Here the plasticity of resin, which increases flexibility of composites around the margins, has been restricted when compared to composite shrinkage stress analysis (Peris *et al.*, 2003). Shinohara *et al.* (2001) factors which prevent flex and increase flexural strength should be applied more extensively in order to help avert marginal leakage.

Kleverlaan & Feilzer (2005) observed that polymerization shrinkage, condensation stress, elastic modulus, and flow are significant factors in determining the ultimate properties of the resin composite.

Floyd & Dickens (2006) report that changes to the resin base such as an increase in the base monomer can provide increased flexural strength and decreased volumetric shrinkage of composites. Replacing the Bis-GMA or TEGDMA by UDMA also create an increase in flexural strengths of the resin matrix. This might be explained by the degree of conversion of the polymer matrix or the capability of the urethane linkage to form hydrogen bonds in the copolymer. Limited sliding of the polymer segments relative to each other is presumed to cause the resultant increase in flexural strength (Floyd & Dickens, 2006).

Zandinejad *et al.* (2006) sought improvements from the filler component rather than the resin and found that composites containing glass ceramic fillers improved flexural strength and modulus significantly more than conventional glass fillers. The incorporation of nanoalumina particles also led to increased flexural strength of composites. The wear performance of the composites did not however correlate with the mechanical properties, although a positive correlation between wear resistance and impact strength was observed (Zandinejad *et al.*, 2006).

Tanimoto *et al.* (2006) establish that flexural strength of composite resins reduced with increasing filler particle size. Since dental composites cannot resist heavy occlusal forces, many methods have been introduced to reinforce them, such as using fibers or whiskers as reinforcing agents (Xu *et al.*, 2003). Similar results were observed by Papadogiannis *et al.* (2007) who discovered that compressive strength, hardness, flexural strength and modulus of elasticity all increased and shrinkage decreased when the filler volume fraction of dental composites was increased.

Fischer *et al.* (2004) showed that biting forces higher than the fracture resistance of glass fiber reinforced composites can occur during the mastication process. This highlights the need to maximise the flexural strength of dental composite materials while maintaining a hard restorative structure.

The flexural strength is determined by design principles that optimize both tooth and composite thickness. Nagasiri & Chitmongkolsuk (2005) showed that the likelihood of long term endurance increased with larger aggregates of coronal tooth structure remaining, with endodontically treated molars. This might be because not only the flexural strength but also the stiffness of a material increases as the thickness of the material increases (Anusavice, 2003).

Design considerations for dental composites are mainly dependent on the need for suitable space that will permit adequate stiffness of the restoration, as well as the need for adequate retention and resistance to dislodging forces on cementation (Nissan *et al.*, 2001). Flexibility of composites is especially significant since flexural forces on the unsupported top-middle area of the bridge will incline to displace the most extreme mesial and distal margins of the bridge. The area of the margin affected may change depending on the direction of the force. However, the concentration of stress will still be related to the marginal area. Poor analysis regarding the influence of flexibility (Vaidyanathan, J. & Vaidyanathan, T.K. 2001; Vaidyanathan *et al.*, 2003) on composite margin integrity demarcates knowledge on optimum bridge design. Studies to date do not appear to analyse the influence of flexibility of composite materials on marginal integrity in order to improve bridge design. The need to decrease flexibility is however, acknowledged by Visvanathan *et al.* (2007) who report that, improving flexural modulus and flexural strength will yield better marginal integrity. The flexibility of the bridge and the influence on the marginal seal can be envisioned as viewing forces acting on a beam (representing a bridge) hung between two stands (representing the tooth support of the bridge).

2.4.3 Microhardness of dental composites

Hardness is usually correlated with the physical properties such as mechanical strength, flexibility and resistance to intra oral softening (Uhl *et al.*, 2003). The surface hardness of composites is influenced by various factors, including, organic matrix composition, type and amount of filler particles and degree of conversion (Correr *et al.*, 2005).

Several direct and indirect methods can be used to assess the degree of polymerization of resin composites. As the direct methods are complicated and expensive, the indirect methods such as visual examination, a scrape test, and hardness, evaluation are more appropriate (Bouschlicher *et al.*, 2004; Poskus *et al.*, 2004).

Dewald & Ferracane (1987) compared four indirect methods and established that the visual and scraping methods correlated well, but seriously overrated depth of cure as compared with surface hardness tests or a degree of conversion analysis. Furthermore, some studies, has found that surface hardness values exhibit a positive correlation with the degree of conversion (Bouschlicher *et al.*, 2004).

The surface hardness experiments require the use of a static diamond tip under a specific load, over a tested material and over a specific period of time, which shapes an indent after removal of the load. This indent is microscopic and in a Vickers hardness test, the shape resembles a pyramid square shaped impression (Poskus *et al.*, 2004). The Vickers hardness number (VHN) is calculated by dividing the load by the surface area of the indentation. The lengths of the diagonals of the indentation are measured and average values are obtained

and the VHN is read from a table. The drawback of this test is that it is not suitable for the measurement of materials which are resilient, as they tend to recover, rendering the indentation inaccurate (Poskus *et al.*, 2004).

Lappalainen *et al.* (1989) reported that there was no relationship between hardness and abrasion resistance of composites. Kawai *et al.* (1998) found that a direct relationship exists between the surface hardness and the wear resistance of unfilled resins.

2.5 Influence of oral environment on mechanical properties

The warm, wet nature of the mouth sets a clear demand for filled resin restorative materials as well as, all other dental restorative materials in order to maintain reasonable stability in such conditions. However, it is well established that exposure of dental resin composites to an aqueous environment decreases their mechanical properties (Mohsen & Craig, 1995) and their resistance to wear (De Gee *et al.*, 1990). These reductions have been attributed to the hydrolytic degradation of the polymer matrix and of the filler (Oysaed & Ruyter, 1986), and to water induced filler matrix bond failure (Soderholm *et al.*, 1996).

The main causes of failure of filled resin restorations, that is inadequate wear resistance, marginal sealing, and (to a lesser extent) inadequate color stability have also been related with poor solvent stability (Qvist *et al.*, 1986). Thus, long term survival of dental resin composite within an oral environment is evidently of great concern. Previous studies of the compartment of resin dental composites in a moist environment have mainly been conducted in water with a few in some other liquids, for example, ethanol (Ferracane & Berge, 1995), food simulating liquids (Krishnan & Yamuna 1998), and sodium hydroxide (Sarkar, 2000), expectedly with the purpose of mimicking the effects of saliva or temporary environmental challenges. To date, little is known about the behavior of resin dental composites in artificial saliva. However, Soderholm *et al.* (1996) have ascertained that dental resin composites leached more ions on being exposed to artificial saliva than to water, casting doubt on the clinical relevance of the use of water as the aging medium and echoing previous concerns (Darvell, 1978).

Both physical and chemical processes affect the degradation of dental composites in the oral cavity (Ferracane & Berge, 1995; Gopferich, 1996). Chemical degradation of dental composites can be caused by hydrolysis and/or enzyme catalysis from saliva and enzymes in the oral environment, weakening the composite material sufficiently to reduce restoration longevity and mechanical properties (Santerre *et al.*, 2001). Degradation changes the composite microstructure by forming pores or openings from which degradation products, residual monomers and oligomers can be released (Gopferich, 1996).

Degradation of the dental composites in the oral conditions can proceed by hydrolysis of the silane bond (Zhou *et al.*, 2006). Hydrolysis of ester bonds in the composite is another degradation pathway. The majority of resin elution studies have been done in water to simulate the oral environment (Sideridou & Achilias, 2005). Water diffuses into the composite and accumulates at the interface between the resin and filler material, reacting with the silane and filler material to release degradation products into solution. Water diffusion can also release unreacted resin monomers into the solution (Geurtsen, 1998).

Research groups have investigated the leaching of organic components from commercial dental composites when aged under various environments (Ferracane, 2006; Geurtsen, 1998). However, commercial dental composites contain initiators, stabilizers, inhibitors, and various additives that might be proprietary and/or vary with manufacturer. This complex composition critically complicates the study of chemical degradation in commercial dental composites.

Artificial saliva is a liquid with a complex composition, which simulates the conditions of the oral environment to combine an analysis of the behavior of dental materials not only under occlusal forces, but also considering the complexity of the oral environment (Tornavoi *et al.*, 2012). In the oral cavity, dental composite materials must resist contact with saliva. Some authors have studied the effects of fluids (artificial saliva, deionized water) on the mechanical properties of resin based composites (Okada *et al.*, 2001; Musanje & Darvell, 2003).

2.6 Ultrasonication

The big challenge encountered in synthesis inorganic nanoparticle composites is that the nanoparticles cannot be dispersed in resin matrix at the nano level by conventional techniques because the surface energy of the nano particles is very high, and these particles tend to agglomerate during mixing (Xia *et al.*, 2001). The physical stability and *in vivo* distribution of nanoparticles are affected by their mean size, polydispersity, and surface charge density (Tang *et al.*, 2003).

Ultrasonication is a common technique for the preparation and processing of polymer nanoparticles. It is particularly effective in breaking up aggregates and in reducing the size and polydispersity of nanoparticles (Tang *et al.*, 2003).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

In this chapter, the materials selection, preparation, fabrication, and testing methods are described. The raw materials include the inorganic fillers, resin monomers and chemical additives. The mechanical testing methods include methods to determine flexural strength, wear resistance and microhardness. The material characterisation methods include SEM, TEM and FTIR.

3.2 Experimental design

The study involved three components:

- The material design component, which involved trial-and-error in order to produce TiO₂ nanocomposites for comparative analysis;
- The experimental component which provide data on wear, flexural strength and surface hardness of the TiO₂ nanocomposites prepared, and control composite materials;
- Comparative components which include experimental characterisation analysis in order to make recommendations regarding the overall performance of the nanocomposite materials evaluated.

The resin matrix UDMA was divided into 12 groups. See Table 3.1. The monomer matrix was mixed with 10 wt % of nano-TiO₂, of three different particles sizes 5 nm, 21 nm and 80 nm. The UDMA matrix was used as a monomer according to control commercial composites.

Each group was treated with MPTMS, of three different concentration 2.5, 10 and 30 wt %. This silane compound was used to improve the adherence of resin to filler surfaces.

In series D, the SR Adoro® composite was used as an experimental control. Nano-TiO₂ was added to reinforce the control and to provide the desired filler loading for each specimen group.

Table 3.1: Design of the study groups showing the different sized of nano-TiO₂ used, and the concentration of silane (MPTMS) used, with UDMA and also showing the control groups.

Group	Matrix	Nano-TiO ₂ size	Silane (MPTMS) wt%
A ₁	UDMA	5 nm	none
A ₂	UDMA	5 nm	2.5
A ₃	UDMA	5 nm	10
A ₄	UDMA	5 nm	30
B ₁	UDMA	21 nm	none
B ₂	UDMA	21 nm	2.5
B ₃	UDMA	21 nm	10
B ₄	UDMA	21 nm	30
C ₁	UDMA	80 nm	none
C ₂	UDMA	80 nm	2.5
C ₃	UDMA	80 nm	10
C ₄	UDMA	80 nm	30
D ₁	Control	5 nm	none
D ₂	Control	5 nm	2.5
D ₃	Control	21 nm	none
D ₄	Control	21 nm	2.5
D ₅	Control	80 nm	none
D ₆	Control	80 nm	2.5
D ₇	Control sample		

3.3 Sample preparation

3.3.1 Introduction

The interface between the nanoparticles and surrounding matrix is critical because it governs the structural integrity and long term performance of the nanocomposites. Consequently, the nanoparticles are surface modified with an organic layer to render them compatible with the matrix polymer and there by prevent aggregation.

Ultrasonication is a non-impact method to de-agglomerate particles or to increase dissolution time, by breaking intermolecular interactions. The de-agglomeration is achieved through acoustic cavitation (the formation, growth and collapse of bubbles).

In this study the sample preparation procedure was divided into two stages. See Figure 3.1:

- The first stage commenced with the surface treatment of the nano-TiO₂ powder;
- The second stage involved the incorporating the nano-TiO₂ into a resin matrix UDMA and the control sample.

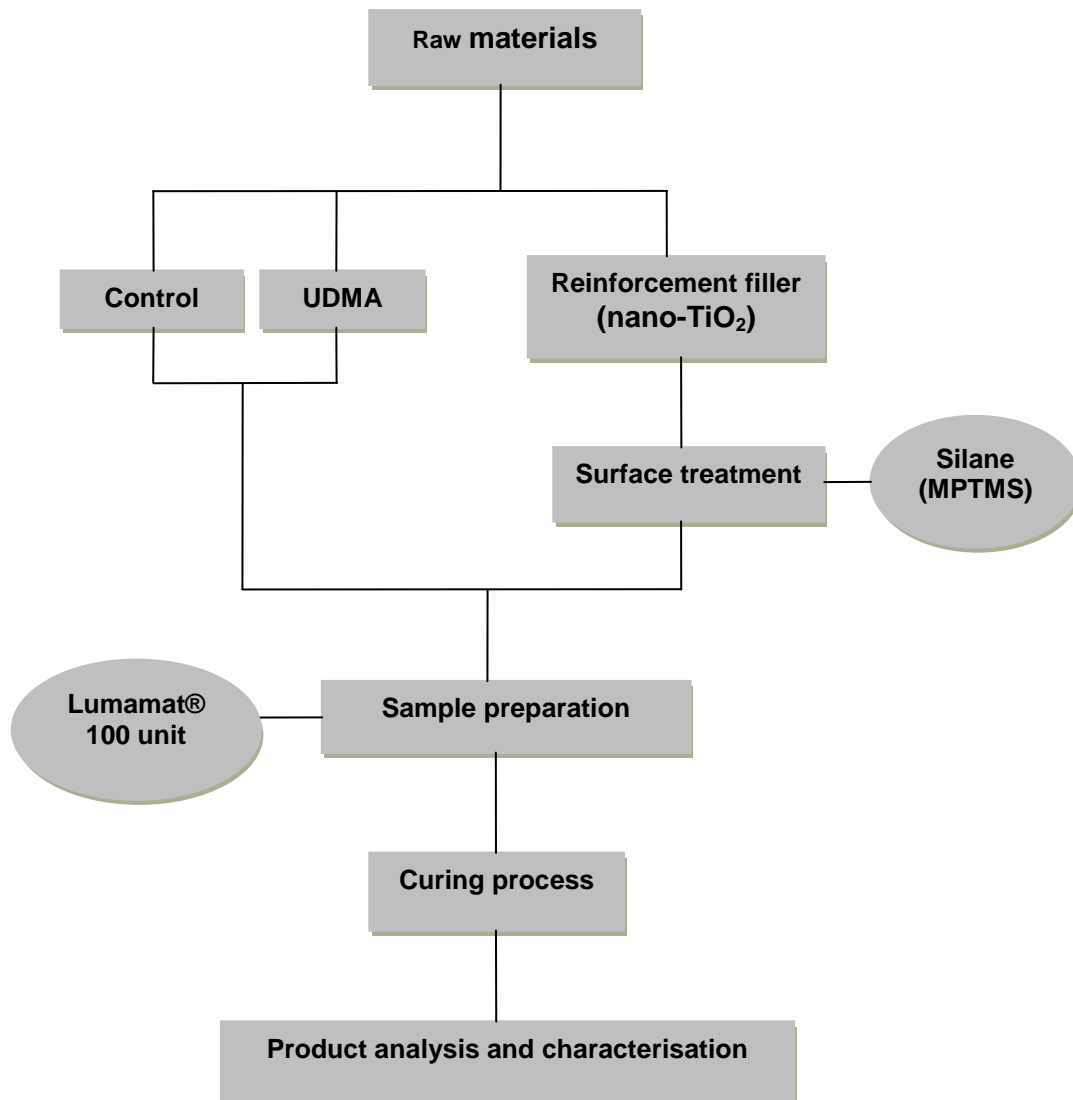


Figure 3.1: Illustrate procedure that was followed in the preparation of samples

3.3.2 Chemicals

The nano-TiO₂ particles were obtained from various suppliers as indicated in Table 3.2 below.

Table 3.2: Nano-TiO₂ particles

No	Average particles size (nm)	Supplier	Trade product name	Country of origin
1	5	TiPE	PC-5	China
2	21	Evonik	P-25	Germany
3	80	NELSA	Trial product	South Africa

The resin matrix UDMA and MPTMS were obtained from Sigma Aldrich (Johannesburg, South Africa). The SR Adoro® product, Ivoclar Vivadent, was obtained from Vivodent (Cape Town, South Africa).

Curing instrumentation combined light with an electronically controlled heater. With the controlled light/heat tempering process, the optimum material properties of the control veneering material could be achieved. The Lumamat® 100 is a component of the control system and is used to cure and temper the composite. The lamp radiates light at 400-580 nm, which initiates curing of the material. The commercially available light sources used for photocuring produce visible radiation in the blue region of spectrum 480 nm. In order to meet these criteria it is necessary to develop the most effective, safe photoinitiating system. Photoinitiating system for dental applications is based on camphorquinone (CQ) and various amines such as (2-dimethylaminoethyl) methacrylate (DMAEMA), and many others. CQ and DMAEMA were obtained from Sigma Aldrich (Johannesburg, South Africa) and were used as received from the supplier.

3.3.3 Surface treatment of nano-TiO₂

The surface treatment of nano-TiO₂ was performed by mixing MPTMS in xylene in the presence of 2 wt % by volume of n-propylamine used as catalyst, then nano-TiO₂ (Figure 3.2) was mixed with MPTMS, by adding three different concentrations of MPTMS (2.5, 10 and 30 wt %), in separate experiments, to 1 g of nano-TiO₂. Acetic acid was added to the mixture until a pH of 3.3 was reached (Wilson *et al.*, 2007). This mixture was sonicated for 10 min, stirred for 1 hour with a mechanical stirrer, and then centrifuged for 10 min at 10 000 rpm in order to separate the silanised nano-TiO₂ from the solution. Before and after centrifuging, the mixtures was washed with ethanol, the mixture was then placed in an oven at 80 °C for 12 hours to dry. Figure 3.3 shows the three series of nano-TiO₂ (A, B and C) after the surface treatment. The treated and untreated nano-TiO₂ were analysed by TEM and FTIR spectroscopy.



Figure 3.2: Raw nano titanium dioxide (nano-TiO₂)



Figure 3.3: Containers with untreated and treated nano-TiO₂

3.3.4 Preparation of resin composites

The respective series of nanocomposites, namely A, B, and C (based on the particle sizes of the nano-TiO₂ 5 nm, 21 nm and 80 nm), each comprises four further groups, were prepared

by mixing the monomer resin matrix UDMA and 10 wt % of nano-TiO₂ (Behera & Banthia, 2007). The nano-TiO₂ mass ratio was determined by weight. The following chemicals were used: 0.5 wt % CQ as an initiator and 0.5 wt % DMAEMA as an accelerator. The nanocomposite was prepared by mixing with a magnetic stirrer in a glass vessel. The mixture was then cast into a stainless steel templates and covered on both sides (top and bottom) with clear thin glass plates. The dimensions of the specimens were 2 mm x 4 mm x 25 mm. See Figure 3.4. As a comparison with a commercial dental resin composite, the D series contained 7 groups; each group was reinforced with nano-TiO₂ (5, 21 and 80 nm) as shown earlier in Table 3.1.

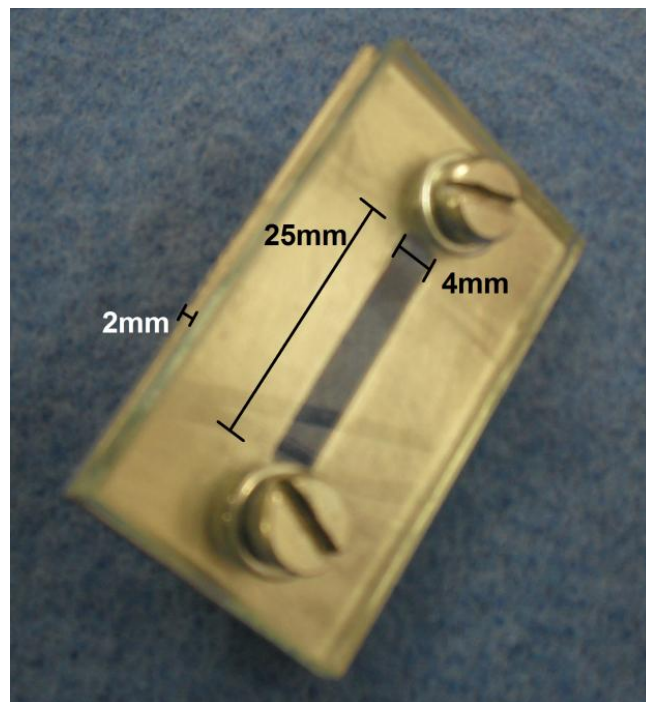


Figure 3.4: Stainless steel template

Specimens were then irradiated in a light curing unit for 60 minute according to manufacturer's instructions of the control. Figure 3.5 shows the instrumentation used, on completion of curing, the specimens were removed from the template and polished using silicon carbide paper ranging from 500 to 2000 grit number. Figure 3.6 shows the prepared sample.

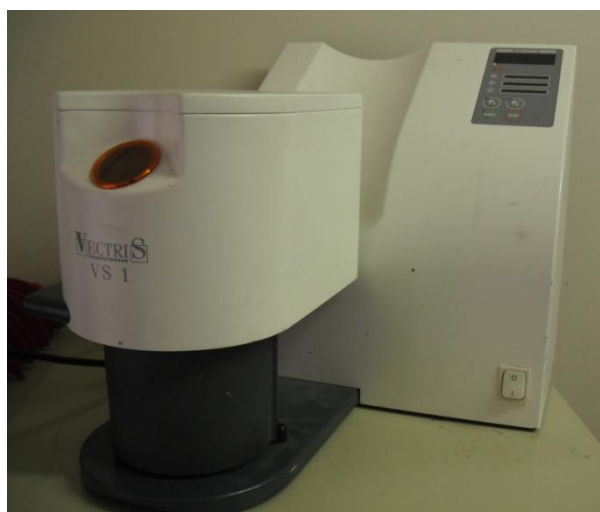


Figure 3.5: The curing instrumentation used in the preparation of the sample

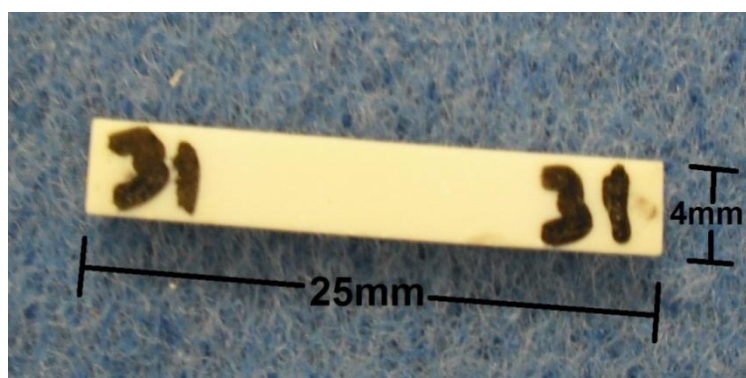


Figure 3.6: Photograph of a prepared sample

3.3.5 Ageing in artificial saliva

In order to better simulate the oral cavity environment, samples were be immersed in artificial saliva (pH 5) at 37 °C for 28 days (Bruno *et al.*, 2011), the composition is given in the Table 3.3 below.

Table 3.3: Composition of artificial saliva

Components	(g/L)
NaCl	0.400
KCl	0.400
CaCl ₂ ·2H ₂ O	0.795
Na ₂ S·9H ₂ O	0.005
NaHPO ₄ ·2H ₂ O	0.780
Urea	1.000
H ₂ O	1.000

3.4 Determination of mechanical properties

3.4.1 Wear resistance (pin-on-disk)

Wear tests were performed using a conventional pin-on-disk machine at the Centre for Materials Engineering at the University of Cape Town, South Africa. The instrumentation is shown in Figure 3.7. Wear tests were performed under reciprocating dry sliding conditions according to the American society for testing and materials (ASTM) G99 – 05 (2010). The rotating speed of the disc was 100 ms^{-1} under ambient *in vitro* conditions. A normal load of 15 N was applied to the test material. After the end of the sliding distances, the testing apparatus was stopped and the surfaces of the samples were cleaned with a brush to remove wear loss materials. The weight loss (in mg) was measured with an electronic balance to a precision of 10^{-5} g to determine the wear of the samples. Wear loss was computed from weight loss measurements taken after 100 m sliding distances.

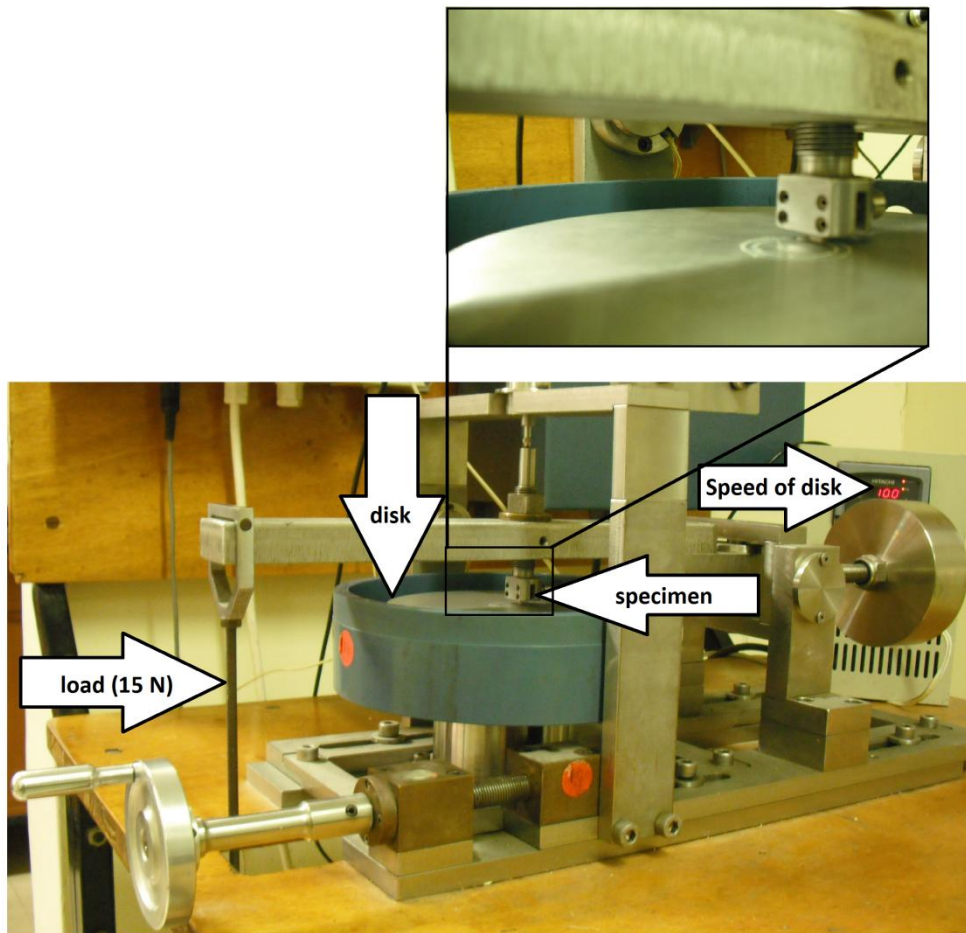


Figure 3.7: Views of the pin-on-disk wear tester showing how the sample wears on the disk

3.4.2 Flexural strength

Flexural strength was determined using 3-point bending tests, using a universal testing machine, Hounsfield H25KS (Redhill, England), operating at 95 % confidence level, at the Department of Mechanical Engineering at Cape Peninsula University of Technology, South Africa. The instrument was set at a constant speed of 6 mm. The initial loading was 5 kN and increased until failure of the specimen. The specimens were placed between two smooth metal plates 20 mm apart, to allow free rotation during the test as shown in Figure 3.8.



Figure 3.8: Instrumentation used for determining flexural strength

3.4.3 Microhardness (VHN)

The surface hardness values of composites are considered to provide an indication of their wear resistance properties. The complexity of the wear process of composites has, however, given rise to conflicting reports regarding the correlation between the surface hardness of a material and its wear resistance. In this study, the surface hardness measurements were carried out by determining the VHN. A Highwood HWDM-3 (TTS Unlimited Inc., Osaka, Japan) instrument at the Centre for Materials Engineering at the University of Cape Town

was used to investigate the relationship between the surface hardness of the dental nanocomposites and their wear resistance. See Figure 3.9.

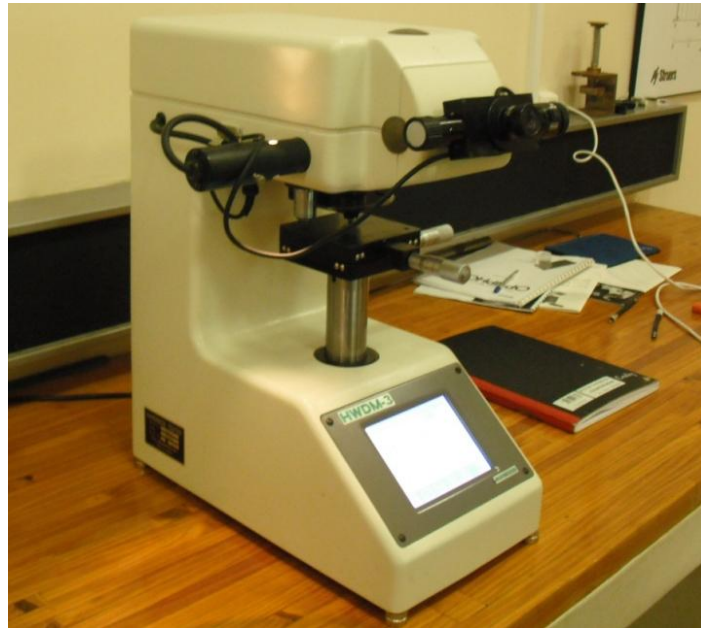


Figure 3.9: Apparatus used to determine the Vickers hardness number (VHN)

3.5 Material characterisation

3.5.1 Scanning electron microscope (SEM)

The morphology of the nanocomposites' fracture surface and distribution of the nano-TiO₂, were determined by SEM. A FEI Nova Nano SEM 230 (Eindhoven, Netherlands) instrument, situated at the Electron Microscopy Unit at the University of Cape Town, was used. See Figure 3.10. Elemental mapping of the titanium was performed using energy dispersive X-ray spectroscopy (EDS).

To obtain microstructural information, SEM, was also performed on the silicon layers. Measurements were performed in secondary electron mode at an accelerating voltage of 15 keV and current of 100 pA. The images were recorded at 34 °C angle and the working height was 5 mm. The particle sizes and distributions from SEM were determined using the Origin 8.0 software associated with the instrument.

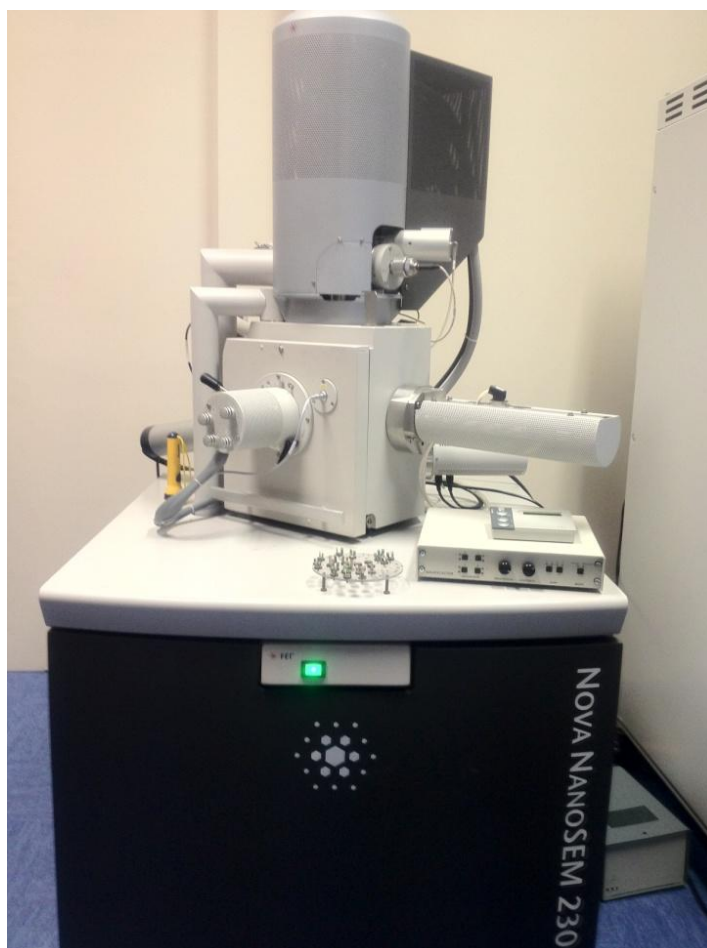


Figure 3.10: Scanning electron microscope (SEM) used in this study

3.5.2 Transmission electron microscopy (TEM)

TEM was used to study the morphology of the specimens (untreated and treated nano-TiO₂) and to identify their particles size. A high resolution transmission electron microscopy, FEI Tecnai G2 20 (Eindhoven, Netherlands) equipped with a Gatan image filter for energy filter imaging and acquiring electron of energy loss spectra at the Electron Microscopy Unit at the University of Cape Town. See Figure 3.11. The instrument was operated at 200 KeV. A suspension of nano-TiO₂ was prepared by diluting the nano-TiO₂ powder with ethanol and ultrasonicated it for 10 min. A drop of suspended sample was placed on a carbon-coated copper grid. The ethanol was subsequently evaporated at room temperature, leaving the nano-TiO₂ on the grid.



Figure 3.11: Transmission electron microscope (TEM) used in the experiment

3.5.3 Fourier transforms infra red spectroscopy (FTIR)

FTIR was used to characterise untreated and treated nano-TiO₂ to establish the chemical structure of the nano-TiO₂ after silane treatment. A spectrum™ 100 Optica (Perkin–Elmer, USA) instrument, shown in Figure 3.12, was used at the Department of Chemistry at the University of Western Cape, South Africa. The following experimental conditions applied: resolution of 2 cm⁻¹ throughout the spectral range (4000 to 500 cm⁻¹) and scanning speed of 0.50 cm s⁻¹.

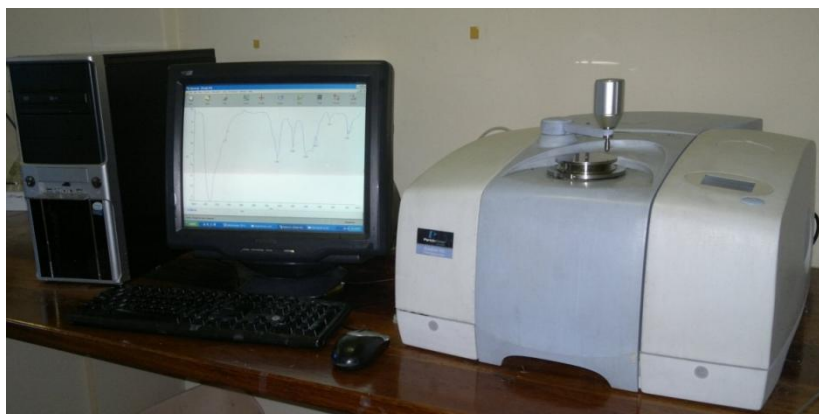


Figure 3.12: Fourier transforms infra red spectrometer (FTIR)

3.6 Statistical analysis

The statistical procedure applied for the determination of the amount of wear, flexural strength and surface hardness, which were the univariate analysis of variation, was carried out using Statistical package for the social sciences SPSS 20 software, IBM SPSS Data Collection (USA), (ANOVA analysis, comparing each group with control). The univariate analysis of variance enabled comparisons of each group with the standard set by control group. The level of significance for all test was = 0.05. The p-values were used to found significant difference in values in order to draw conclusions.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter reports on the results obtained from the experimental analyses and disseminates the information pertaining to achieving the objectives of this study. The discussion is divided into two parts. The first part is related to the treatment of the nano-TiO₂. The second part addresses the nanocomposites' mechanical behaviour due to filler incorporation.

4.2 Surface treatment of nano-TiO₂ particles

4.2.1 Introduction

As mentioned earlier in section 2.2.2.1, nano-TiO₂ is hydrophilic and has a strong tendency of forming the state of agglomeration. The size of these agglomerated particles is larger than the nanoscale due to the extremely large surface area of nano-TiO₂. Nanoparticles tend to strongly agglomerate, hence leading to a decrease in the resultant mechanical properties of the nanocomposite materials (Lin, 2006).

In order to improve the dispersion ability of nano-TiO₂ in the polymer matrix, it is important to reduce the particle size as much as possible before polymerisation. It is also commercially significant to stabilise this suspension of nanoparticles in a nonaqueous solvent. It was expected that the grafted coupling agent MPTMS would form an organic layer on the inorganic nano-TiO₂ surface, which would serve as the compatibiliser for an intermediate medium such as ethanol or a weakly polar medium (Lin, 2006).

Characterisation was carried out using TEM and FTIR. TEM was used to compare the particle size distributions and the particle agglomeration of untreated nano-TiO₂ and treated nano-TiO₂, prepared using the different experimental conditions in deionized water and ethanol solvent. FTIR spectroscopy was first used to identify the qualitative composition of untreated nano-TiO₂ and treated nano-TiO₂.

4.2.2 Confirmation of silane treatment by FTIR

After the treatment of the nano-TiO₂ surface by MPTMS (2.5, 10 and 30 wt %), the surface was investigated by FTIR spectroscopy. FTIR spectra of the surface functionalised nano-TiO₂ particles are shown in Figure 4.1. The nano-TiO₂ exhibited strong absorption peaks at around 1402 and 1654 cm⁻¹, assigned to the =CH₂ stretching vibrations and C=O bending

vibrations, respectively. The absorption peaks between 500 and 800 cm^{-1} are assigned to the vibrations of the Ti–O and Ti–O–Ti framework bonds, respectively (Park *et al.*, 2009). For a treated nano-TiO₂ surface, the characteristic absorption peaks at 3129 cm^{-1} are assigned to the –CH₂ groups of the coupling agent. The MPTMS functionalised nano-TiO₂ particles gave a weak but visible absorption peak at 2523 cm^{-1} , attributed to the Si–H stretch, which is not observed in the absorption spectrum of nano-TiO₂ particles. A Ti–O–Si transmittance peak at 1183 cm^{-1} and C=O vibration peak at 2159 cm^{-1} are found for the treated TiO₂, implying that the coupling agent was bonded onto the nano-TiO₂ surface by covalent bonds. This shows that the immobilisation of MPTMS onto nano-TiO₂ was successful.

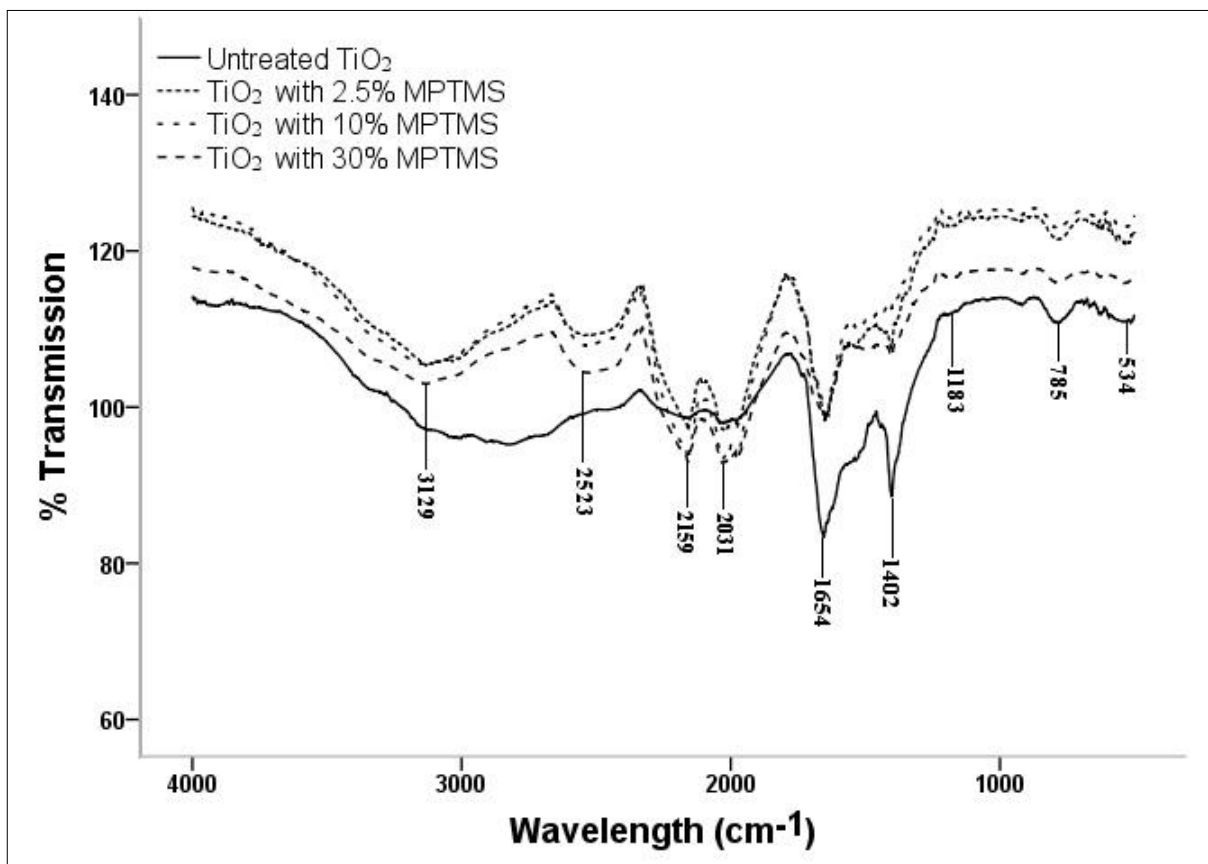


Figure 4.1: FTIR spectra of the untreated and treated nano-TiO₂

4.2.3 Confirmation of silane treatment by TEM

The surface treatment is one of the crucial criteria for developing a successful dental nanocomposite. When the sizes of the filler particles are < 21 nm, aggregation or agglomeration of nano-TiO₂ occurs. See Figure 4.2. With increasing particle size, the agglomeration of particles decreases. Figure 4.3 shows 80 nm TiO₂ without a MPTMS, less

agglomeration than 5 nm 21 nm untreated TiO_2 can be seen. MPTMS was used to reduce agglomeration, enhance filler dispersion and improve the interfacial adhesion between the polymer matrix and fillers. These improvements may also result in the enhancement of the surface and the mechanical properties.

In filled polymers, the elasticity of the nanoparticle chain aggregates appear to contribute to the mechanical properties of the nanocomposite material, indicating that the strength of the inter- particle forces is of importance in a positive way (Bandyopadhyaya et al., 2004). Figure 4.2 shows high agglomeration of untreated nano- TiO_2 (5 nm). Figures 4.4 and 4.5 show TEM images of the nano- TiO_2 without treatment, and with treatment with MPTMS. Less agglomeration of nano- TiO_2 is observed after treatment. Figure 4.5 shows markedly reduced agglomeration.

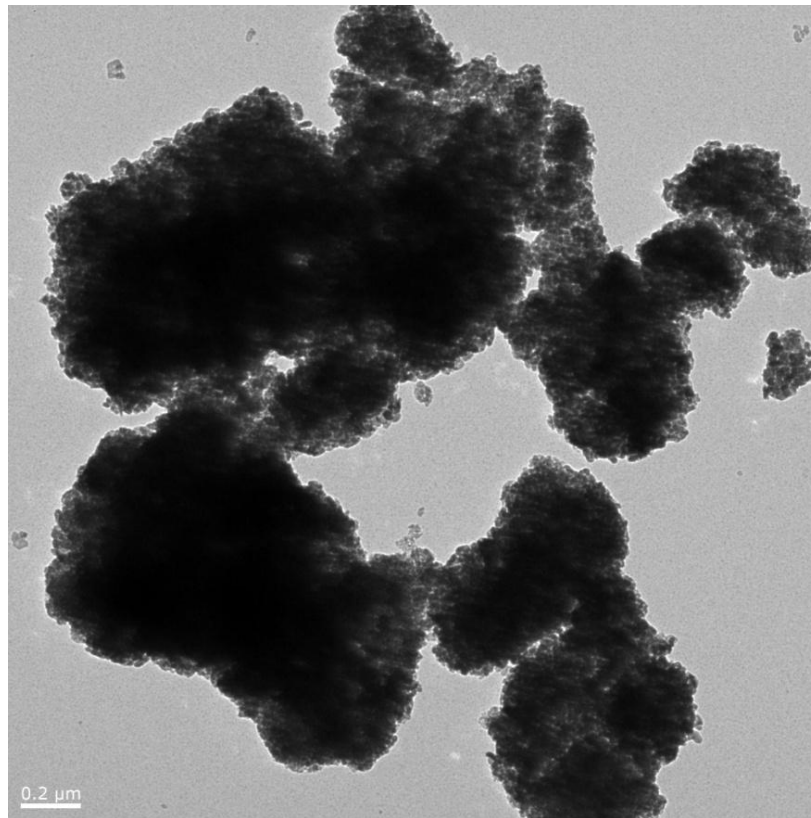


Figure 4.2: TEM image of 5 nm particle size TiO_2 without surface treatment: high agglomeration of TiO_2 can be seen

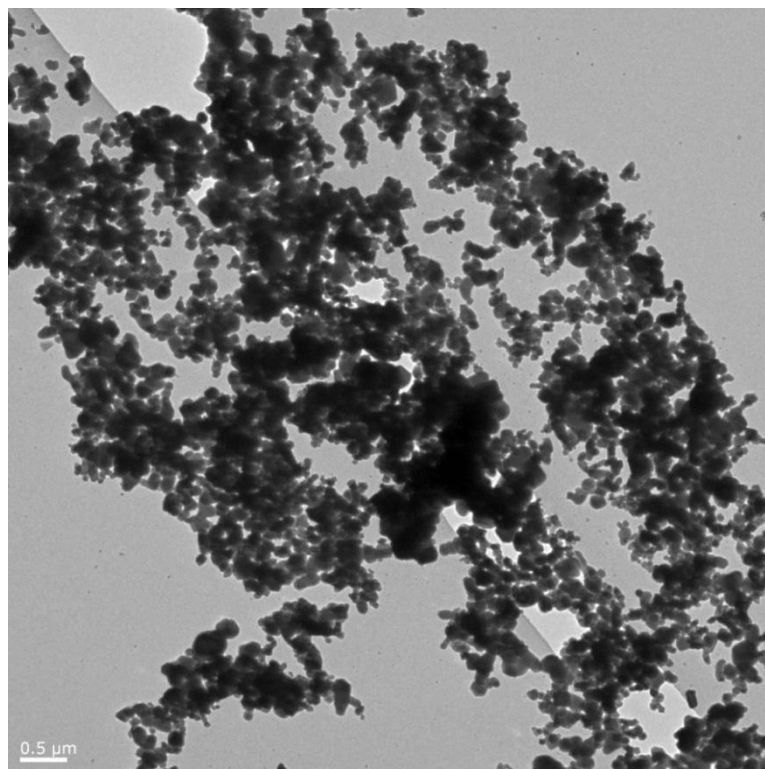


Figure 4.3: TEM image of 80 nm particle size TiO_2 without surface treatment: agglomeration of TiO_2 can be seen

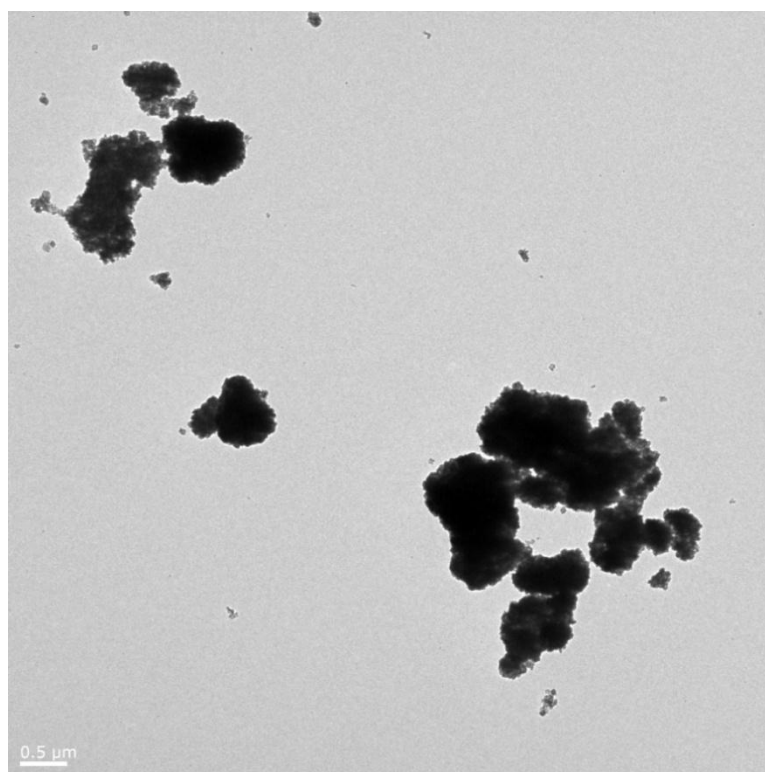


Figure 4.4: TEM image of 5 nm particle size TiO_2 without surface treatment: agglomeration of TiO_2 can be seen

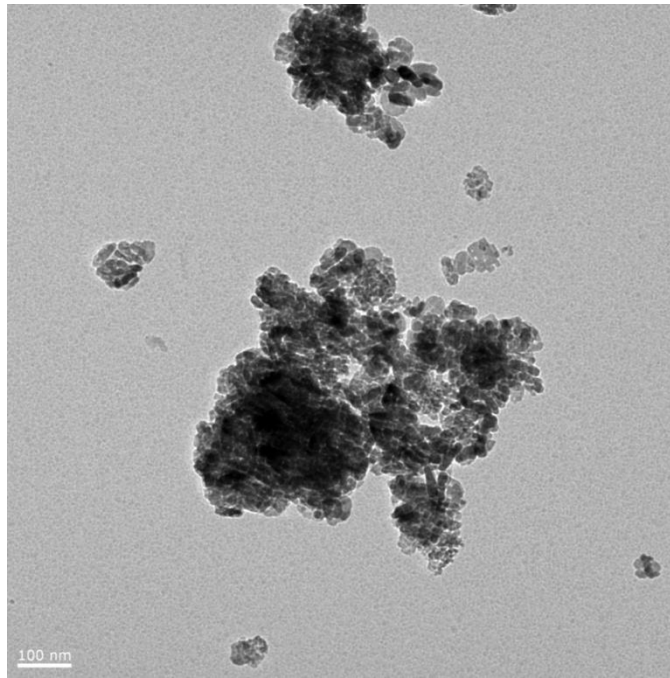


Figure 4.5: TEM image of 21 nm particle size TiO_2 with surface treatment: markedly less agglomeration of TiO_2 can be seen

Figure 4.6 shows agglomeration of nano- TiO_2 (21 nm) after no surface treatment. Figure 4.7 shows markedly reduced agglomeration of nano- TiO_2 (21 nm) after surface treatment. Here, the nano- TiO_2 particles are relatively monodispersed.

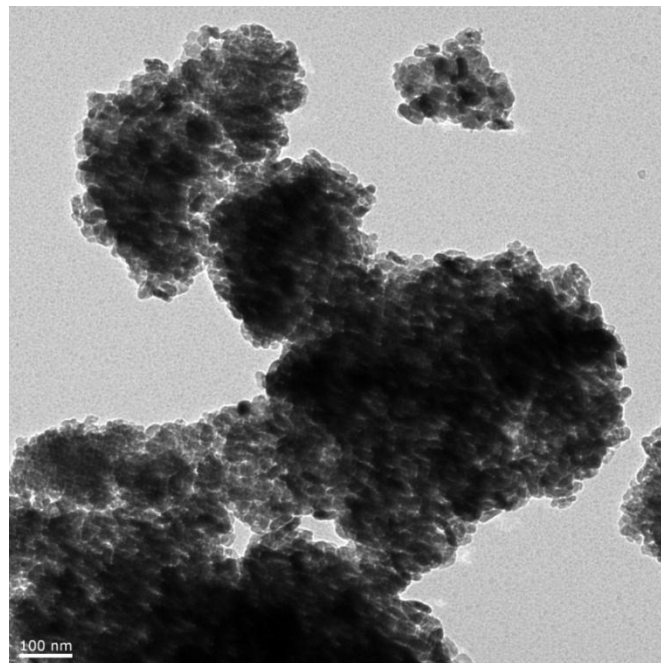


Figure 4.6: TEM image of 21 nm particle size TiO_2 without surface treatment: agglomeration of TiO_2 can be seen

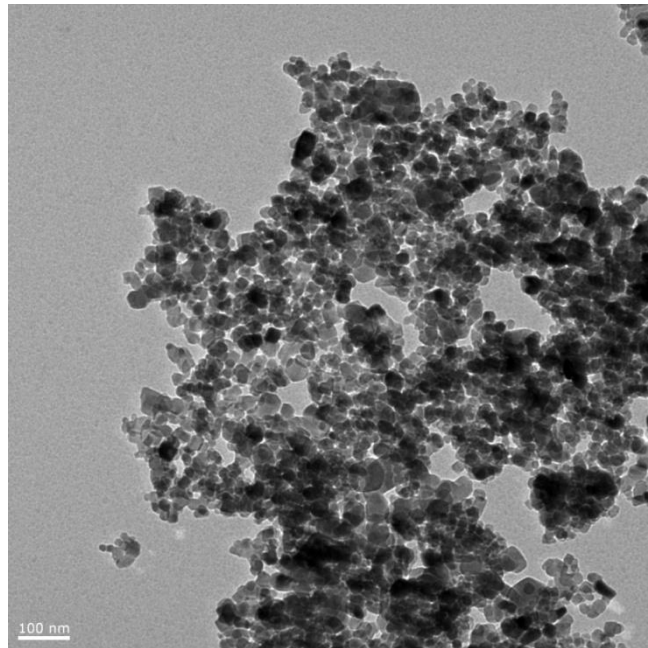


Figure 4.7: TEM image of 21 nm particle size TiO₂ with surface treatment: markedly reduced agglomeration of TiO₂ can be seen and the nano-TiO₂ particles are relatively monodispersed

Figures 4.8 and 4.9 show TEM images of typical examples of untreated and treated TiO₂ (21 nm), respectively. The untreated nano-TiO₂ particles have a much larger size distribution (29.51 ± 19.44 nm) in ethanol than the treated nano-TiO₂ particles (24.12 ± 9.87 nm).

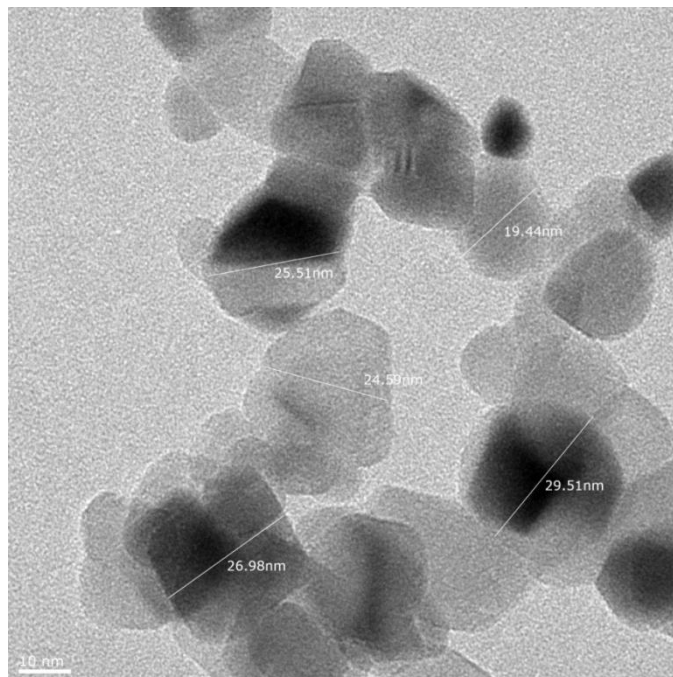


Figure 4.8: TEM image of 21 nm particle size TiO₂ without surface treatment: larger particle size of TiO₂ detected

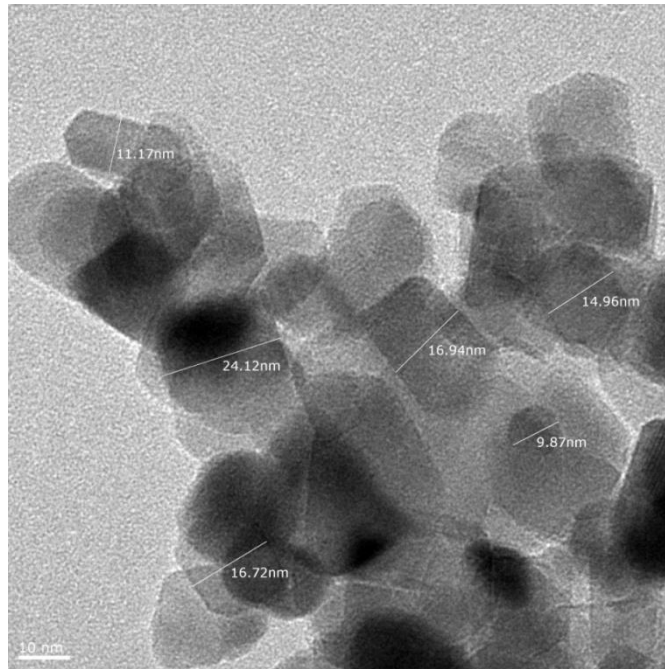


Figure 4.9: TEM image of 21-nm particle size TiO₂ with surface treatment: smaller particles size of TiO₂ detected

4.3 Microscopic investigation

4.3.1 Introduction

Results of the characterisation of the distribution of the nano-TiO₂ in the nanocomposites and reinforced control by SEM and TEM are now presented and discussed.

4.3.2 Scanning electron microscopy (SEM)

The SEM images of fractured surfaces of treated and untreated nanocomposites are now presented. Figure 4.10 indicated that the fracture surface of the treated TiO₂ nanocomposite to be mostly a homogeneous rough surface in which the nano-TiO₂ are evenly distributed.

Chen (2010) showed that the formation of a strong covalent bond between inorganic fillers and the organic matrix is essential for obtaining good mechanical properties in dental composites. Bonding of these two phases is achieved by treated the fillers with a silane coupling agent that has functional groups to link the filler and the matrix chemically. (A typical coupling agent is MPTMS, as used in this study.) One end of the molecule can be bonded to the hydroxyl groups of silica particles, and the other end is capable of copolymerising into the polymer matrix.

Figures 4.10 and Figure 4.11 confirm that there are matrix chains surrounding treated nano-TiO₂ and that the nanoparticles (diameter \pm 80 nm) are relatively uniformly dispersed throughout the entire polymer matrix. They also indicate that there is a good adhesion between organic and inorganic phases and the distance between nano-TiO₂ is much larger

than the diameter of the nanoparticles. Figure 4.12 shows that the untreated TiO_2 nanocomposites show less adhesion between the matrix and the nano- TiO_2 .

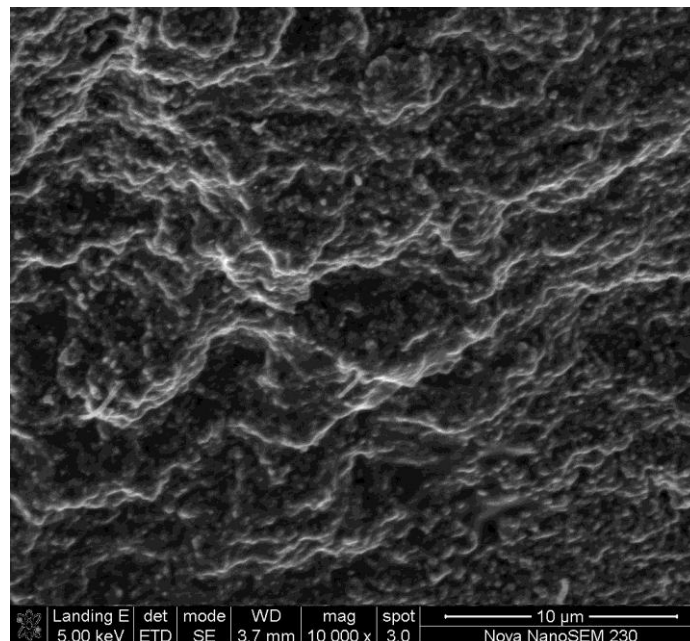


Figure 4.10: SEM of fractured surface of treated TiO_2 nanocomposite (Mag. 10000 \times)

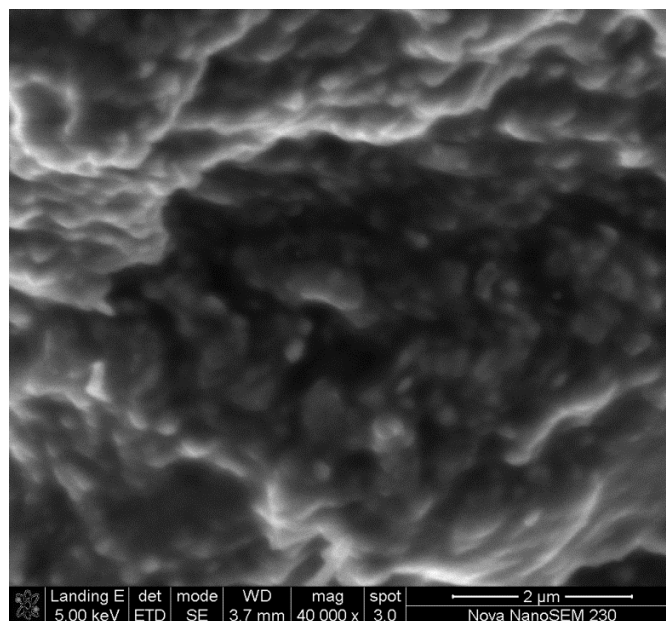


Figure 4.11: SEM of fractured surface of treated TiO_2 nanocomposite (Mag. 40000 \times)

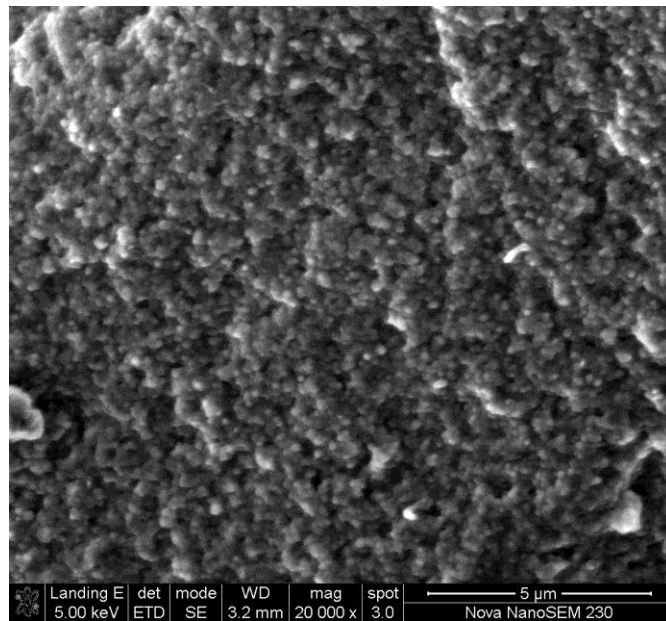


Figure 4.12: SEM of fractured surface of untreated TiO_2 nanocomposite (Mag. 20000 \times)

Analysis by energy dispersive spectrometry (EDS), carried out in conjunction with SEM analysis, revealed that there are Ti and Si elements originating from nano- TiO_2 particles and MPTMS silane coupling modifier present in the sample. See Figure 4.13. This provides further information on the chemical composition of the TiO_2 nanocomposites, and evidence that the treated nano- TiO_2 particles are embedded within the matrix.

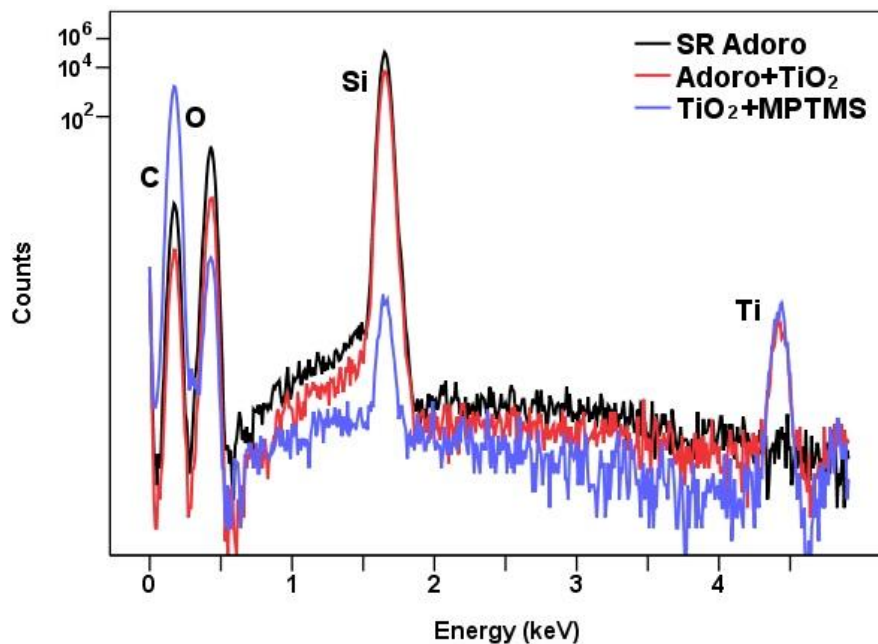


Figure 4.13: EDS spectrum with local quantitative elemental analyses of complete surface of TiO_2 nanocomposites, control and control reinforced with nano- TiO_2

Figure 4.14 shows the EDS spectrum of one such agglomerated particle (the spot shown on the agglomerate was analysed). The peak positions with binding energy for C and Ti can be seen at 0.12 and 4.44 KeV, respectively. No peak for Si is seen, confirming the agglomerates to be untreated particles.

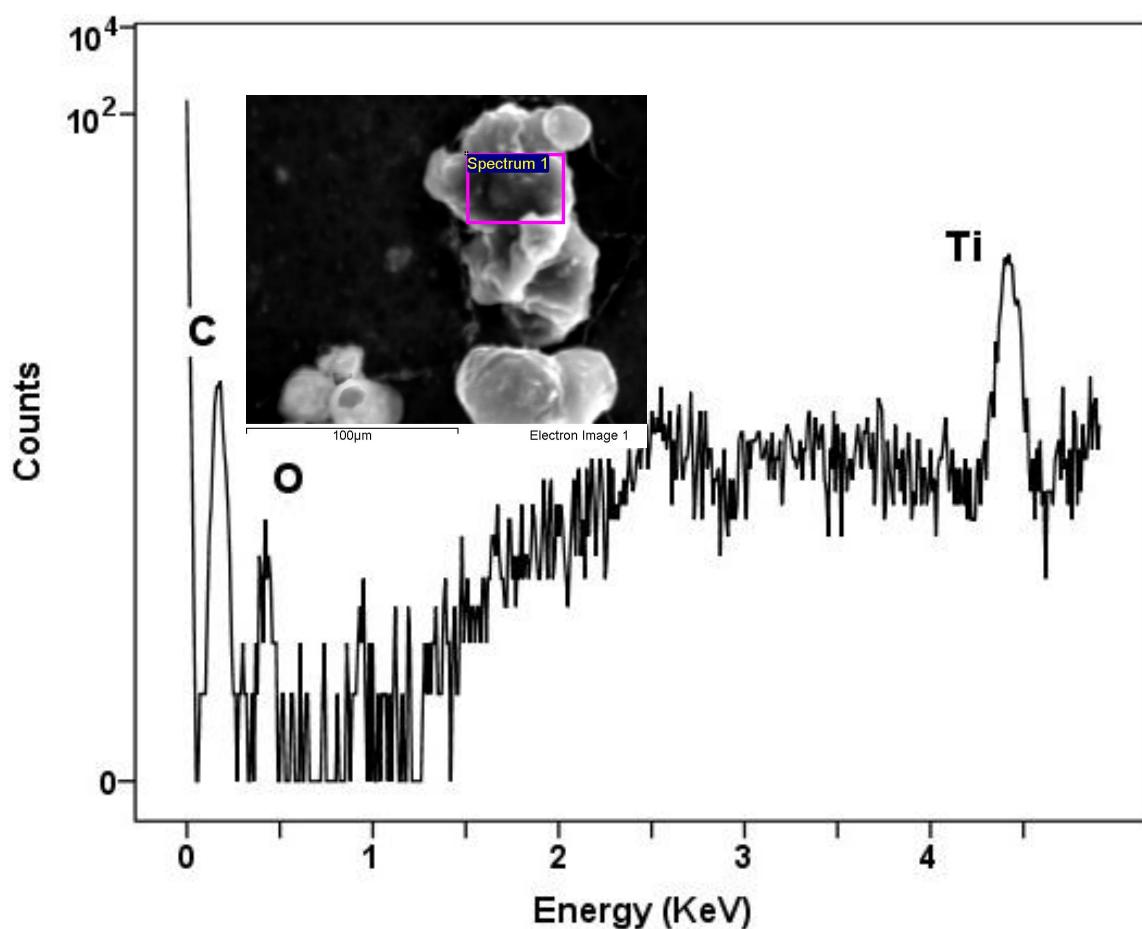


Figure 4.14: EDS spectrum of X-ray emission analysis of agglomerated nano-TiO₂

4.3.3 Transmission electron microscopy (TEM)

Figures 4.15 and 4.16 show TEM images of the TiO_2 nanocomposites without and with treatment, respectively. Less agglomeration of nano- TiO_2 particle was observed in the matrix after treatment.

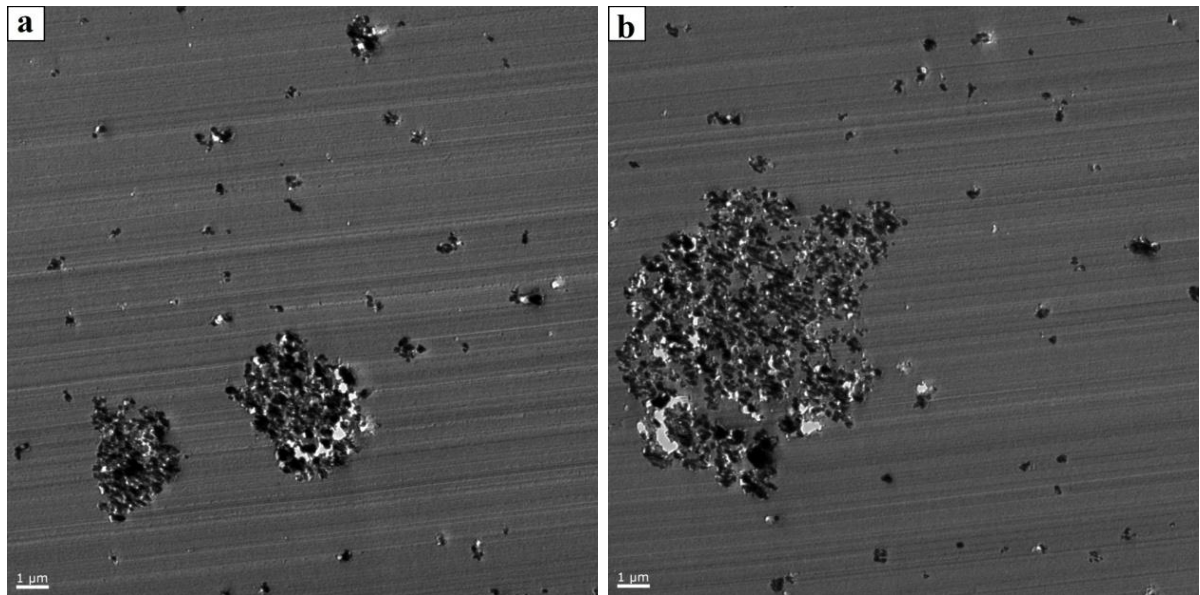


Figure 4.15: TEM images of nanocomposites with untreated 21 nm TiO_2

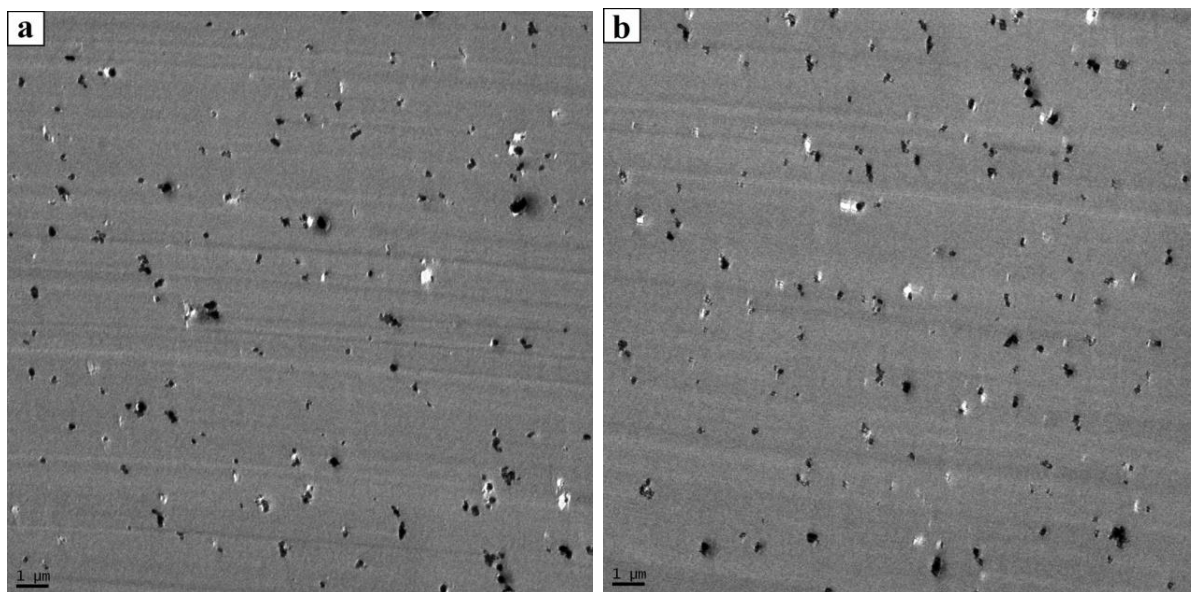


Figure 4.16: TEM images of nanocomposites with treated 21 nm TiO_2

In Figure 4.17, a HR-TEM image of a single nano-TiO₂ particle together with UDMA matrix (TiO₂ nanocomposite) shows a large view of the specimen. A thin amorphous layer about two to three monolayers thick is observed between the nano-TiO₂ surface and the UDMA, indicated by an arrow.

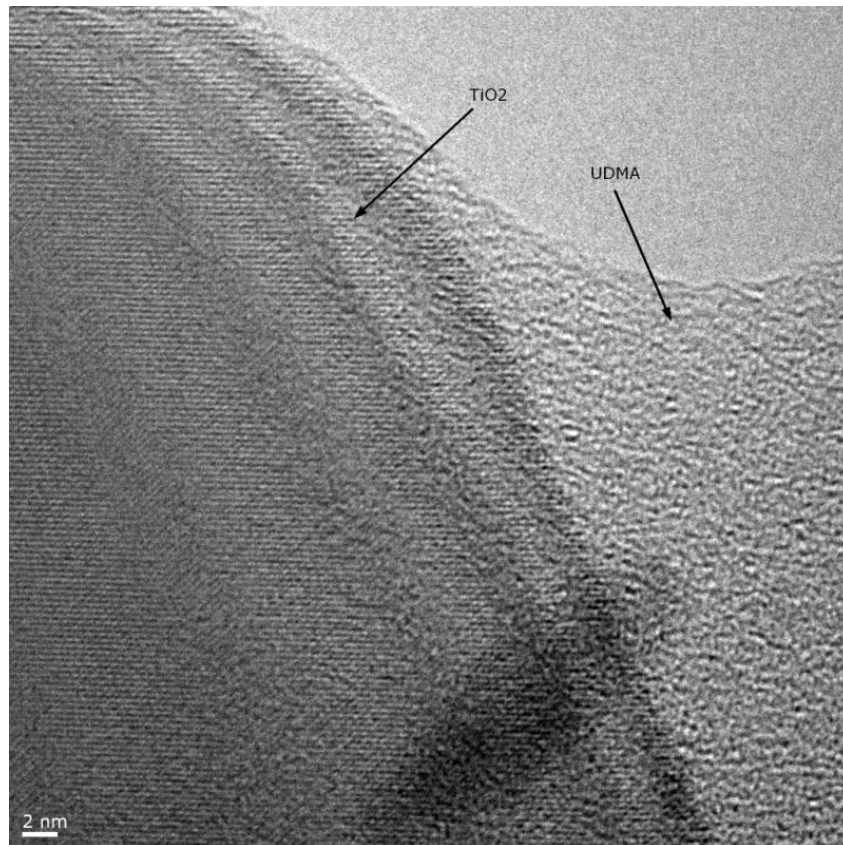


Figure 4.17: HR-TEM image showing the structure of the TiO₂ nanocomposite and the crystalline size

Scientists have performed many studies to improve inorganic fillers in dental composites, and the current tendency is to reduce the size of filler particles from micrometer to nanometer (Condon & Ferracane, 2000). The used of nanoparticles alongside traditional microparticles influences the mechanical and biological properties of dental composites (Gao *et al.*, 2003). Xia *et al*, (2008) found that adding nano-TiO₂ treated with silane to dental composites improves the hardness and flexural strength of dental composites. Figures 4.18 and 4.19 show typical TEM images of the control sample and the control reinforced with 21 nm TiO₂. The SiO₂ microparticles and TiO₂ nanoparticles are well distributed and incorporated into the resin matrix UDMA of the control sample.

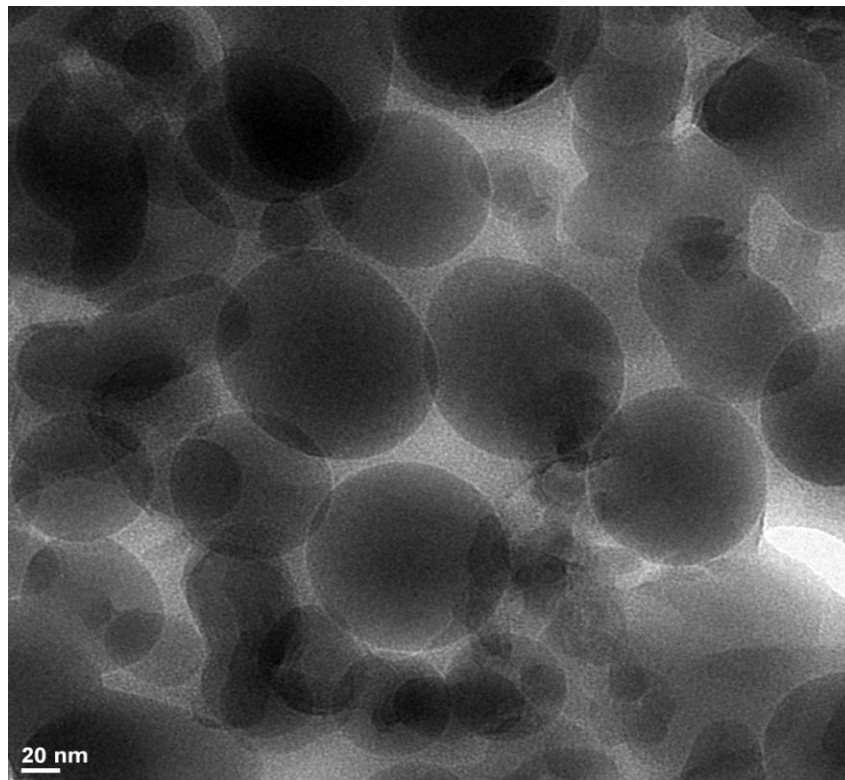


Figure 4.18: TEM image of the control sample

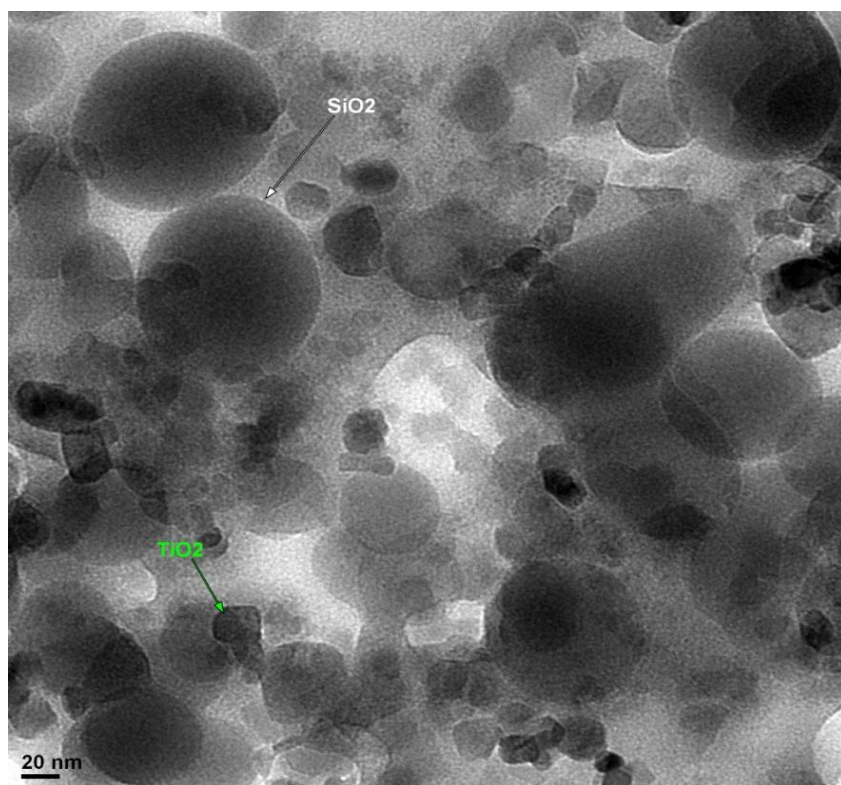


Figure 4.19: TEM image of the control reinforced with 21 nm TiO_2

4.4 Determination of mechanical properties

4.4.1 Introduction

In this section the results of the mechanical properties, wear resistance, flexural strength and surface hardness, of the samples are, presented and discussed.

4.4.2 Wear resistance

The wear resistance test results for all 19 sample groups, including the control group, are summarised in the Appendix. Table 4.1 shows the mean wear loss values (in terms of percentage), standard deviation, median, minimum and maximum wear loss of the control sample group and the 18 TiO₂ nanocomposite groups.

Table 4.1: Comparisons of the wear loss values for each group

Groups	Count	Mean wear loss values (%)	Median wear loss values (%)	Std Deviation wear loss values (%)	Minimum wear loss values (%)	Maximum wear loss values (%)
A ₁ un5 nm	3	19.40	19.36	1.88	17.56	21.32
A ₂ (2.5%) 5 nm	3	12.98	13.11	0.29	12.66	13.19
A ₃ (10%) 5 nm	3	15.81	15.54	0.50	15.50	16.39
A ₄ (30%) 5 nm	3	18.12	18.85	1.45	16.45	19.07
B ₁ un21 nm	3	14.88	14.73	1.62	13.33	16.58
B ₂ (2.5%) 21 nm	3	9.02	8.72	0.55	8.69	9.67
B ₃ (10%) 21 nm	3	12.74	12.84	0.84	11.85	13.53
B ₄ (30%) 21 nm	3	14.14	14.67	0.97	13.02	14.75
C ₁ un80 nm	3	11.33	11.22	1.86	9.53	13.25
C ₂ (2.5%) 80 nm	3	7.66	7.63	1.43	6.24	9.12
C ₃ (10%) 80 nm	3	12.67	12.40	0.54	12.31	13.30
C ₄ (30%) 80 nm	3	11.76	10.99	2.24	10.00	14.30
D ₁ control (un5 nm)	3	9.16	9.16	0.30	8.87	9.47
D ₂ control (5 nm)	3	7.78	7.88	0.36	7.39	8.09
D ₃ control (un21 nm)	3	5.25	5.08	0.56	4.78	5.88
D ₄ control (21 nm)	3	5.16	5.06	0.36	4.86	5.56
D ₅ control (un80 nm)	3	5.30	5.26	0.45	4.87	5.77
D ₆ control (80 nm)	3	3.78	3.78	0.50	3.28	4.28
D ₇ control sample	3	6.89	6.89	0.60	6.30	7.50

The effect of the amount of MPTMS silane added to the nanocomposite containing 5 nm TiO₂ is shown in Figure 4.20. The group which shows less weight loss value provides more wear resistance. From the figure it is clear that the addition of MPTMS silane increases the wear resistance. We believe that this is due to the better bonding of the treated TiO₂ to the UDMA matrix. As the percentage of MPTMS silane was increased the wear resistance decreased hence the TiO₂ nanocomposite with 2.5 wt % showed highest wear resistance.

The effect of the amount of MPTMS silane added to the matrix containing 21 nm TiO₂ is shown in Figure 4.21, and for the 80 nm TiO₂ is shown in Figure 4.22. The same trend was also observed as for the nanocomposites containing 5 nm TiO₂ as discussed above. ($p < 0.01$). Therefore, the effect of the concentration of MPTMS silane on the wear resistance of TiO₂ nanocomposites was significant.

From the three figures we can conclude that the 80 nm size TiO₂ gives higher wear resistance compared to 5 nm and 21 nm nano-TiO₂ particles.

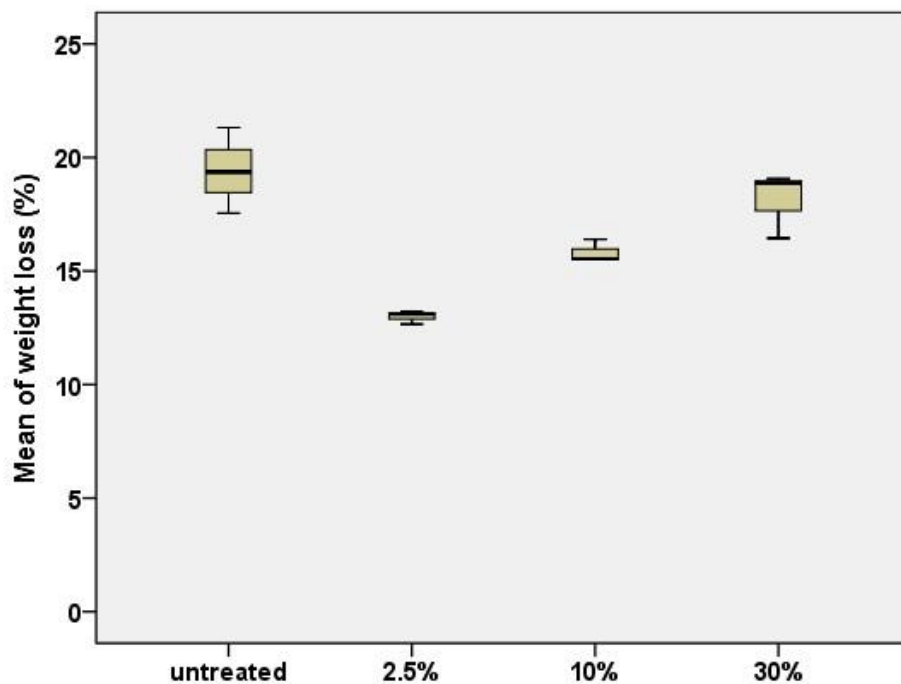


Figure 4.20: Mean of wear loss value (%) of 5 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

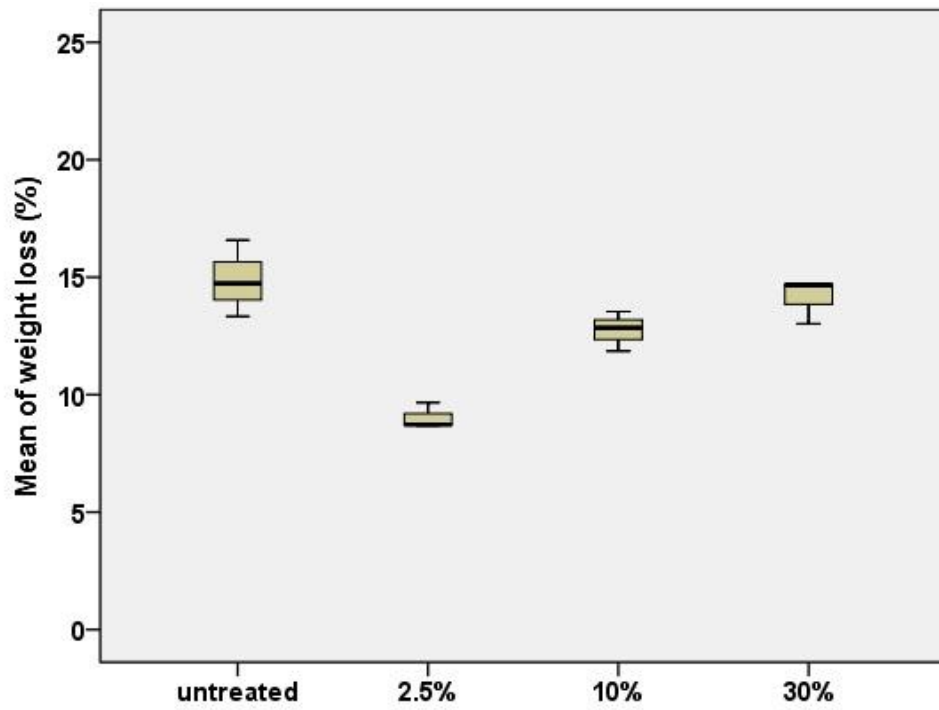


Figure 4.21: Mean of wear loss value (%) of 21 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

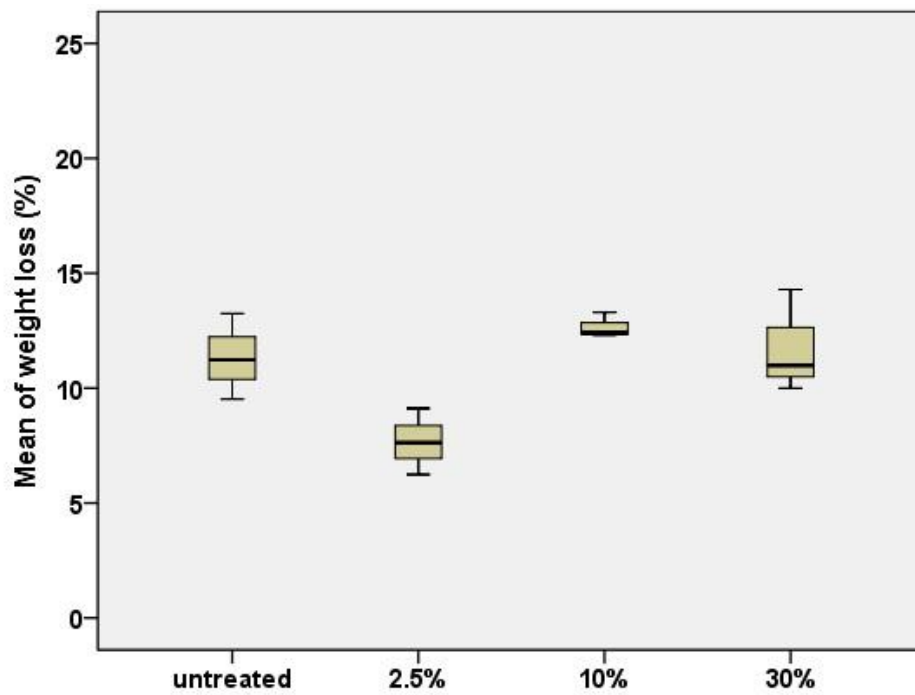


Figure 4.22: Mean of wear loss value (%) of 80 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

In Figure 4.23, the control reinforced with treated 80 nm TiO₂ showed much better wear resistance than any of the other specimens. The control reinforced with untreated 5 nm TiO₂ particles demonstrated higher wear loss values when compared to the other reinforced and unreinforced control. The control which was reinforced with treated nano-TiO₂ showed higher wear resistance than those which were reinforced with untreated TiO₂.

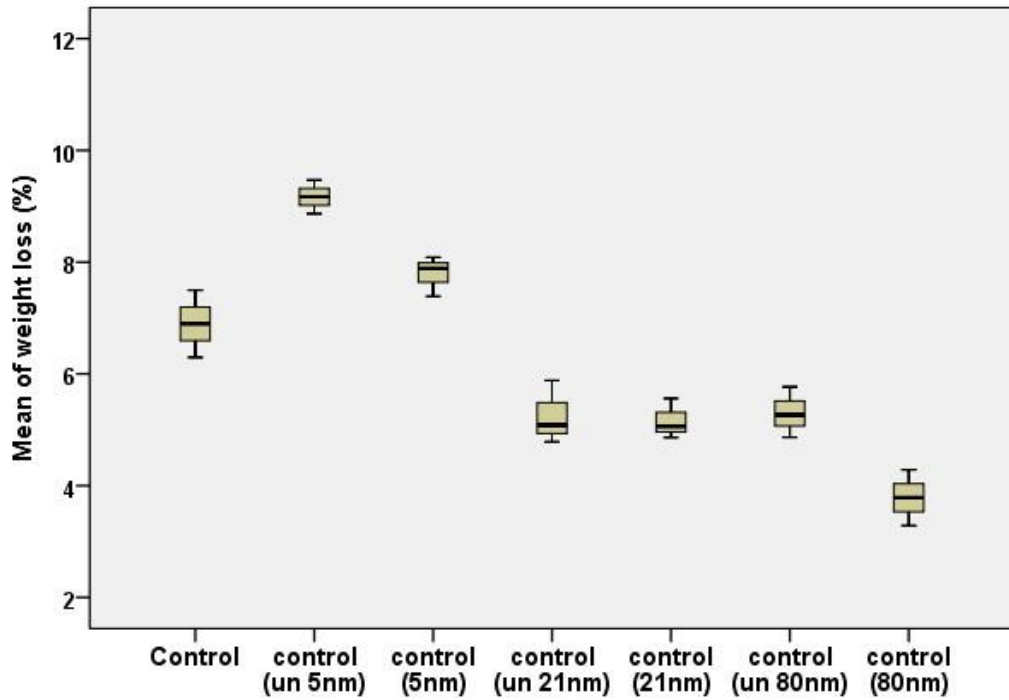


Figure 4.23: Mean of wear loss value (%) of the control reinforced with untreated and treated 5 nm, 21 nm and 80 nm TiO₂

4.4.3 Flexural strength

The flexural strength test results for all 19 sample groups, including the control group, are summarised in the Appendix. Table 4.2 depicts the mean value, standard deviation, minimum and maximum for flexural strength (MPa) of the control sample group and 18 TiO₂ nanocomposites sample groups.

Table 4.2: Comparisons of the flexural strength (MPa) for each group

Groups	Count	Mean flexural strength (MPa)	Median flexural strength (MPa)	Std Deviation flexural strength (MPa)	Minimum flexural strength (MPa)	Maximum flexural strength (MPa)
A ₁ un5 nm	3	89.69	90.70	6.41	82.81	95.50
A ₂ (2.5%) 5 nm	3	102.5	102.3	0.86	101.7	103.4
A ₃ (10%) 5 nm	3	114.5	112.0	4.46	111.8	119.6
A ₄ (30%) 5 nm	3	112.6	109.8	6.46	108.0	120.0
B ₁ un21 nm	3	107.1	107.0	4.81	102.3	111.9
B ₂ (2.5%) 21 nm	3	110.3	110.5	1.04	109.18	111.2
B ₃ (10%) 21 nm	3	100.2	110.5	2.51	98.09	103.0
B ₄ (30%) 21 nm	3	91.37	91.65	2.97	88.27	94.21
C ₁ un80 nm	3	111.4	110.0	5.88	106.4	117.9
C ₂ (2.5%) 80 nm	3	117.2	118.1	2.60	114.2	119.3
C ₃ (10%) 80 nm	3	95.00	95.68	5.60	89.21	100.3
C ₄ (30%) 80 nm	3	94.20	95.70	3.24	90.47	96.40
D ₁ control (un5 nm)	3	95.59	95.79	0.81	94.69	96.29
D ₂ control (5 nm)	3	97.65	97.65	0.60	97.05	98.25
D ₃ control (un21 nm)	3	96.46	96.50	0.65	95.80	97.10
D ₄ control (21 nm)	3	99.65	99.99	0.66	98.89	100.0
D ₅ control (un80 nm)	3	120.7	120.7	0.70	119.9	121.3
D ₆ control (80 nm)	3	134.5	134.5	0.70	133.8	135.2
D ₇ control sample	3	113.6	113.7	0.61	112.9	114.1

Figure 4.24 shows the effect of MPTMS coupling agent on flexural strength of 5 nm TiO₂ nanocomposites. It was observed that the flexural strength was slightly higher when TiO₂ nanocomposite was treated with 10 wt % of MPTMS saline compared to those treated with 2.5 wt % and 30 wt % MPTMS. The flexural strength of treated TiO₂ nanocomposites is higher than the untreated nanocomposite. This is due to the better bonding of the treated TiO₂ to the UDMA matrix.

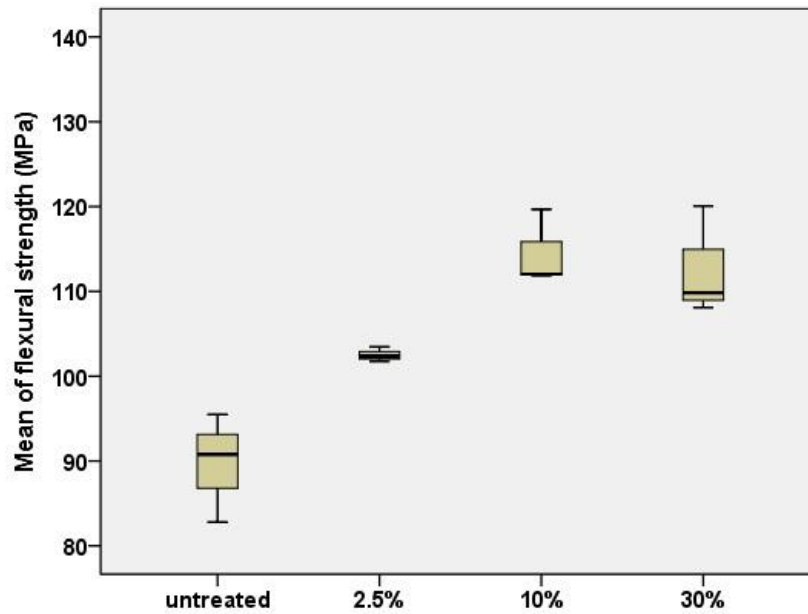


Figure 4.24: Mean of flexural strength (MPa) of 5 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

Figures 4.25 and 4.26 show the flexural strength of nanocomposites containing 21 nm and 80 nm TiO₂, respectively. The graphs show that the flexural strength decreased with increase in MPTMS silane concentration. The p-value was not significant (p=0.20) because it is greater than 0.05. Therefore, the effect of the concentration of MPTMS on flexural strength of the specimens was not significant.

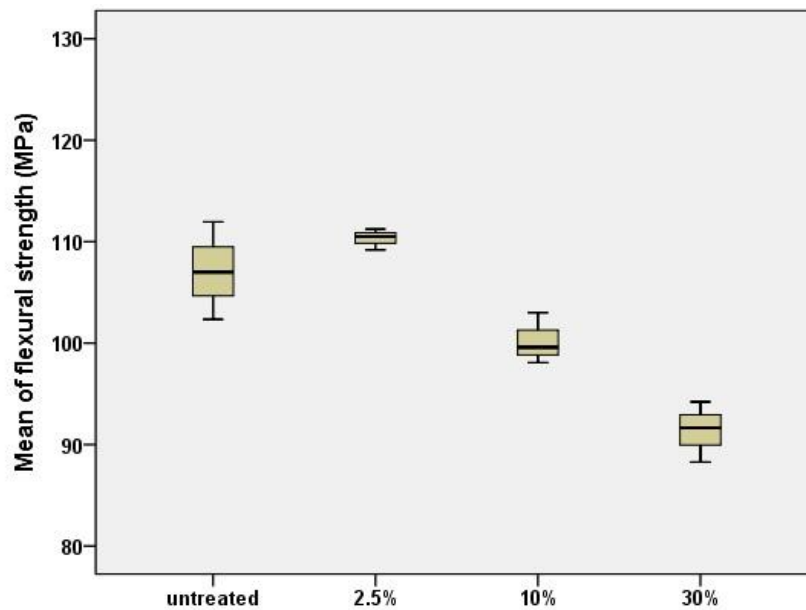


Figure 4.25: Mean of flexural strength (MPa) of 21 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

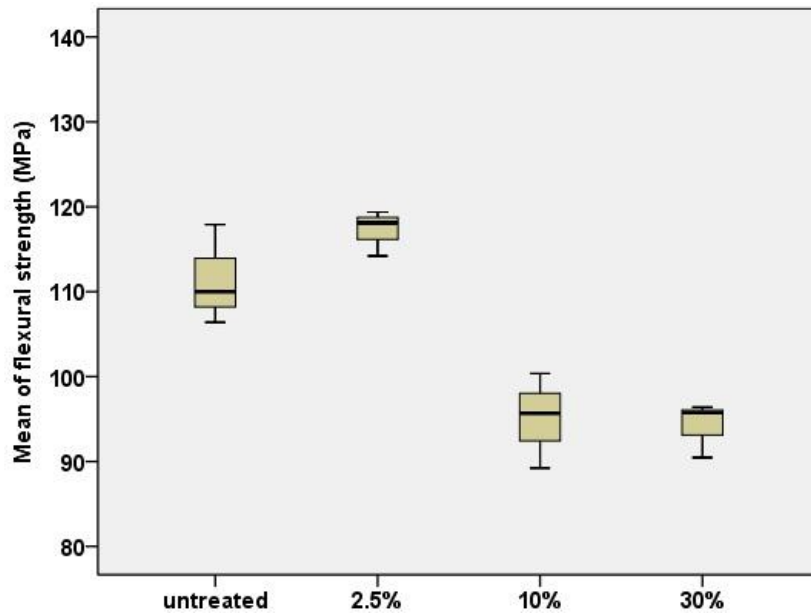


Figure 4.26: Mean of flexural strength (MPa) of 80 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

Figure 4.27 depicts the flexural strength of the control reinforced with untreated and treated 5, 21 and 80 nm TiO₂. The control reinforced with untreated 80 nm TiO₂ had the highest flexural strength, while the unreinforced control showed less flexural strength compared to other controls which were reinforced with nano-TiO₂.

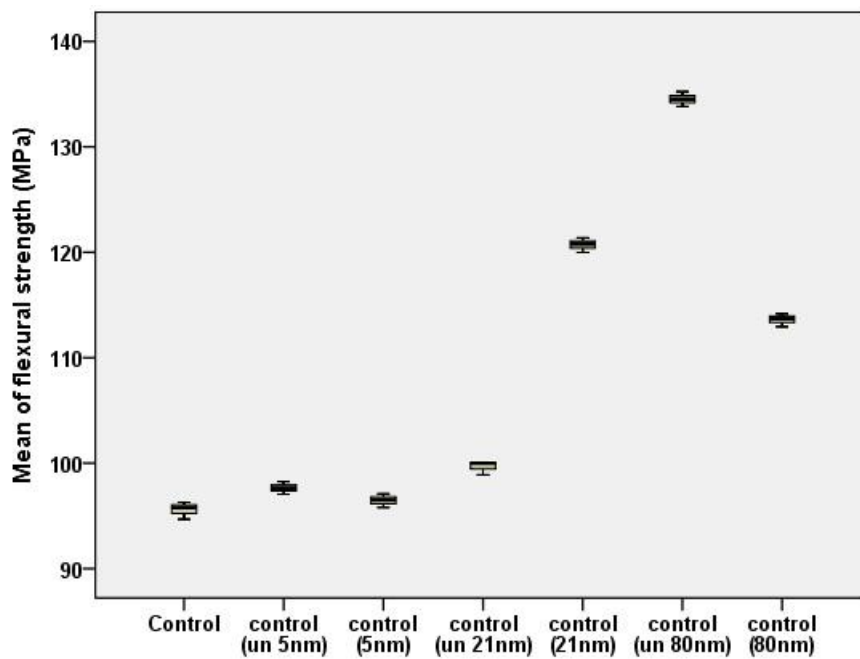


Figure 4.27: Mean of flexural strength (MPa) of the control reinforced with untreated and treated 5 nm, 21 nm and 80 nm TiO₂

4.4.4 Microhardness

The surface hardness values of all the samples are given in the Appendix. The mean values of the surface hardness for each group are shown in Figures 4.28, 4.29 and 4.30. The surface hardness of the 80 nm TiO₂ nanocomposites showed higher surface hardness than 5 and 21 nm TiO₂ nanocomposite. Surface hardness values of the treated TiO₂ nanocomposite with 2.5 wt % of MPTMS were higher compared to those which were treated with 10 wt % and 30 wt % of MPTMS. The p-value was significant: $p < 0.001$. However, the effect of the concentration of MPTMS silane on the surface hardness of specimens was significant.

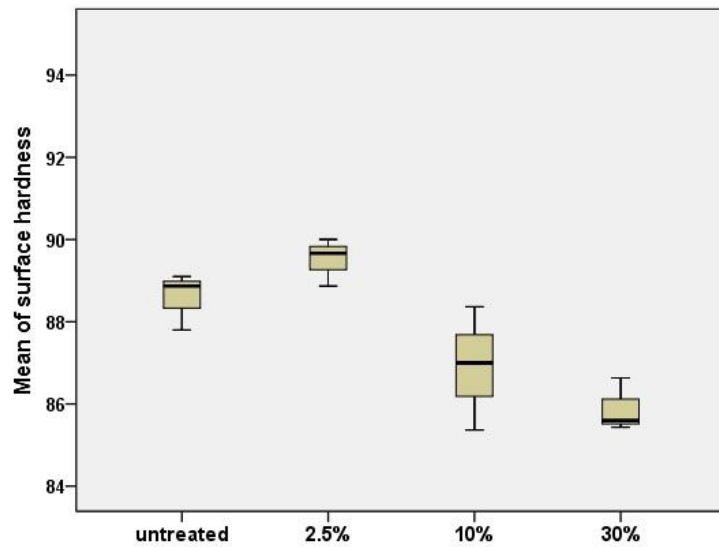


Figure 4.28: Mean of surface hardness value of 5 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

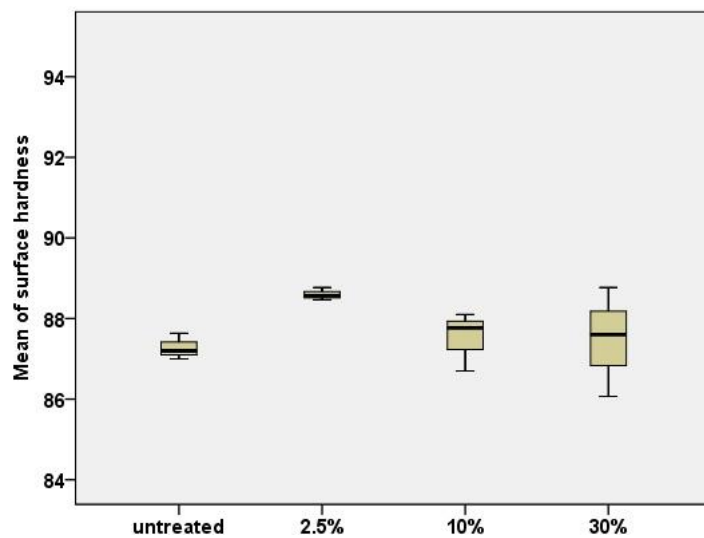


Figure 4.29: Mean of surface hardness value of 21 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

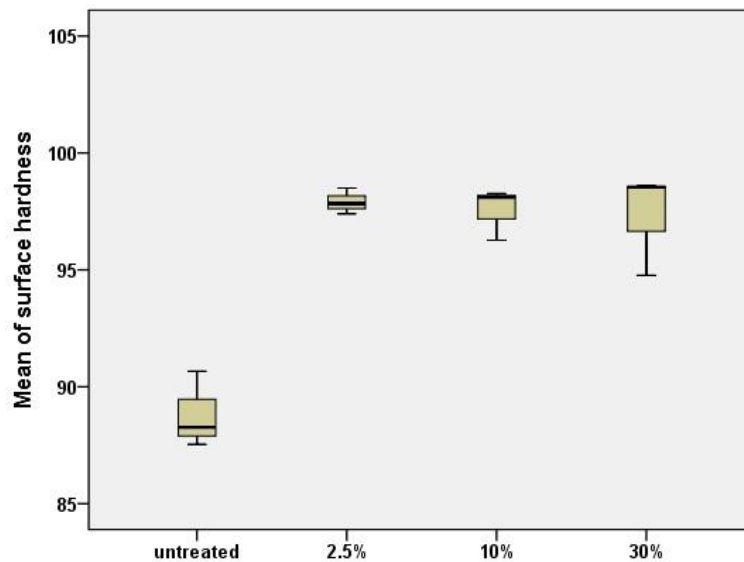


Figure 4.30: Mean of surface hardness value of 80 nm TiO₂ nanocomposites treated with 2.5, 10 and 30% MPTMS

Figure 4.31 shows the effect of particle size of TiO₂ and addition of MPTMS silane on the surface hardness of the control composite. When we compare the nano-TiO₂ particles of different sizes 5 nm 21 nm and 80 nm, as the size of the particles increases the surface hardness also increases. We believe that the small particles give a low surface hardness because they tend to agglomerate due to their high surface energy. We also noted that the addition of treated TiO₂ to the control composite increases the surface hardness. For example, the surface hardness of the control reinforced with untreated 5 nm increased when MPTMS silane was added. This is because the MPTMS silane is an adhesion promoter (Antonucci *et al.*, 2005; Xia *et al.*, 2008).

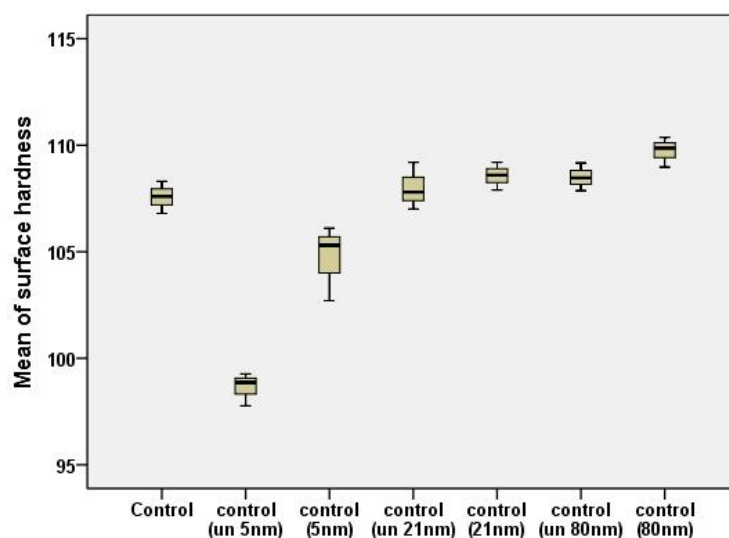


Figure 4.31: Mean of surface hardness value of the control reinforced with untreated and treated 5 nm, 21 nm and 80 nm TiO₂

In this study we found that treated TiO₂ nanocomposite exhibited significantly lower wear loss, higher flexural strength and higher surface hardness than the untreated TiO₂ nanocomposite, this is in agreement with literature which says that the average filler size and silane coupling agent, have a significant effect on the mechanical properties of nanocomposite materials (Manhart *et al.*, 2000; Sabzi *et al.*, 2009). The optimum concentration of MPTMS seems to be that of 2.5 wt %. Higher concentrations of MPTMS did not improve the properties of TiO₂ nanocomposites (Karabela & Sideridou, 2011). At lower silane concentrations (2.5 wt %) the silane molecules must have a parallel orientation relative to the particle surface. At higher silane concentrations (10 and 30 wt %) silane molecules form a layer around the filler particles which now have to occupy a random, parallel and perpendicularly orientation relative to the particle surface. Wear resistance and surface hardness showed a maximum value for the TiO₂ nanocomposite contained 2.5 wt % MPTMS. Some studies have revealed a negative correlation between surface hardness values and the wear resistance of dental composite (Faria *et al.*, 2007; Manhart *et al.*, 2000). The findings of the present study are in disagreement with the latter; in the present study, TiO₂ nanocomposites with higher surface hardness values showed higher wear resistance. As for the effect of particle sizes, the samples containing treated 80 nm TiO₂ which were less agglomerated particles showed better mechanical properties than those containing 5 nm or 21 nm TiO₂.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Overall conclusion

The treatment of nano-TiO₂ particles was carried out prior to fabrication of experimental dental nanocomposites. Their properties were evaluated; samples were compared to each other. The filler particle size and particle distribution had significant effects on the nanocomposites' mechanical properties.

Surface treatment of nano-TiO₂ particles with MPTMS has effects on wear resistance, flexural strength and surface hardness of the dental nanocomposites. However, direct addition of untreated nano-TiO₂ particles into the UDMA, resulted in their poor dispersion and resulting low mechanical properties of dental nanocomposites. The surface treatment of nano-TiO₂ particles decreases the agglomeration between the nanoparticles and also improves their wear resistance, flexural strength and surface hardness in the dental nanocomposites. As for the effect of particle sizes, the samples containing smaller nano-TiO₂ which were more agglomerated particles showed low mechanical properties. However, a positive correlation between surface hardness values and the wear resistance was observed. Treated TiO₂ nanocomposites with the highest surface hardness values showed the highest wear resistance. The control reinforced with treated nano-TiO₂ particles had better mechanical properties than the control reinforced with untreated nano-TiO₂ particles.

5.2 Specific conclusions

5.2.1 Introduction

Here, specific conclusions are presented in separate property; categories based the results of the respective mechanical tests. Conclusions regarding the effect of the concentration of MPTMS used on the surface of the nano-TiO₂, and the size of the nano-TiO₂ are given. Further investigations of reinforcement control with nano-TiO₂ are concluded.

5.2.2 The effect of nano-TiO₂ on wear resistance

From the wear resistance results of TiO₂ nanocomposites and control reinforced with nano-TiO₂ particles specimens the following can be concluded:

1. Introducing a MPTMS bond between the nano-TiO₂ particles and the UDMA in order to reduce the agglomeration of nano-TiO₂ particles was successful with the 80 nm particles. The wear resistance of TiO₂ nanocomposites decreased with increasing concentration of the MPTMS coupling agents.

2. Treated 80 nm TiO₂ showed significantly improved in wear resistance in comparison with the treated 5 nm and 21 nm nano-TiO₂ particles, which showed more agglomeration.
3. A control reinforced with 80 nm nano-TiO₂ particles had significantly increased wear resistance, compared to the control composite and other control reinforced with 5 nm and 21 nm of nano-TiO₂.

5.2.3 The effect of nano-TiO₂ on flexural strength

From the flexural strength results of TiO₂ nanocomposites and control reinforced with nano-TiO₂ particles specimens, the following can be concluded:

1. The flexural strength of the 21 nm and 80 nm TiO₂ nanocomposites decreased with increasing MPTMS silane concentration. While the 5 nm TiO₂ nanocomposites had higher flexural strength with 10 wt % of MPTMS. Little information was obtained for the silane nano-TiO₂ particles bonding mechanism.
2. TiO₂ nanocomposites with 5 nm TiO₂ particles resulted in significantly lower flexural strength for all evaluated materials.
3. The flexural strength of a control reinforced with 80 nm TiO₂ was significantly improved compared to the control composite and other control specimens, with 5 nm or 21 nm TiO₂.

5.2.4 The effect of nano-TiO₂ on surface hardness

From the microhardness results of TiO₂ nanocomposites and control reinforced with nano-TiO₂ particles specimens the following can be concluded:

1. The surface hardness of TiO₂ nanocomposites treated with 2.5 wt % of MPTMS had higher surface hardness values compared to samples that were treated with higher concentrations of MPTMS.
2. Dental nanocomposites with 5 nm TiO₂ particles had significantly lower surface hardness values than all the other nanocomposites materials evaluated.
3. A control composite reinforced with 80 nm TiO₂ had significantly improved surface hardness compared to the other control specimens, reinforced with 5 nm and 21 nm TiO₂.

5.3 Recommendations

Based on finding of this study the following are recommended:

1. A common and fundamental problem in nanocomposites is the large extent of agglomeration of the nanoparticles due to their high surface energy. Therefore, new techniques to control de-agglomeration and possibly further organisation of these high aspect ratio agglomerated nanoparticles in polymeric materials needed to be developed to produce de-agglomerated nano-TiO₂ particles at the early synthesis stage, which should result in a homogeneous distribution of particles in the composites.
2. Investigations should be carried out to further improve the wear resistance and flexural strength of TiO₂ nanocomposite by using different resins matrixes (such as Bis-GMA and TEGDMA), curing techniques, nano-TiO₂ volume and adhesive bonding agents.
3. *In vivo* studies are needed to support laboratory data, in order to provide evidence that TiO₂ nanocomposites may can meaningfully provide a useful service for the patients and improve the tooth and restoration longevity.

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APPENDIX

Appendix: Raw data of the specimens

Nr	Groups	subgroups	Wear loss (%)	Flexural strength (MPa)	Surface hardness
1	5 nm	un 5 nm	19.36	82.81	88.87
2	5 nm	un 5 nm	17.55	95.50	89.10
3	5 nm	un 5 nm	21.32	90.78	87.80
4	5 nm	(2.5%) 5 nm	12.66	102.34	88.87
5	5 nm	(2.5%) 5 nm	13.19	103.46	90.00
6	5 nm	(2.5%) 5 nm	13.11	101.75	89.67
7	5 nm	(10%) 5 nm	15.5	112.03	85.37
8	5 nm	(10%) 5 nm	16.39	119.68	88.37
9	5 nm	(10%) 5 nm	15.54	111.87	87.00
10	5 nm	(30%) 5 nm	18.86	109.84	85.43
11	5 nm	(30%) 5 nm	19.07	120.06	85.60
12	5 nm	(30%) 5 nm	16.45	108.09	86.63
13	21 nm	un 21 nm	14.74	102.34	87.63
14	21 nm	un 21 nm	16.58	111.96	87.00
15	21 nm	un 21nm	13.33	107.00	87.20
16	21 nm	(2.5%) 21 nm	8.72	109.18	88.57
17	21 nm	(2.5%) 21 nm	8.69	111.25	88.47
18	21 nm	(2.5%) 21 nm	9.67	110.50	88.77

19	21 nm	(10%) 21 nm	13.53	99.59	88.10
20	21 nm	(10%) 21 nm	12.85	103.00	87.77
21	21 nm	(10%) 21 nm	11.85	98.09	86.70
22	21 nm	(30%) 21 nm	14.75	88.27	85.77
23	21 nm	(30%) 21 nm	13.02	91.65	86.07
24	21 nm	(30%) 21nm	14.67	94.21	86.60
25	80 nm	un 80 nm	11.23	117.90	88.27
26	80 nm	un 80 nm	13.25	106.40	87.53
27	80 nm	un 80 nm	9.53	110.00	90.67
28	80 nm	(2.5%) 80 nm	7.63	114.22	98.50
29	80 nm	(2.5%) 80 nm	9.12	119.37	97.40
30	80 nm	(2.5%) 80 nm	6.24	118.10	97.83
31	80 nm	(10%) 80 nm	12.31	100.37	98.27
32	80 nm	(10%) 80 nm	13.3	89.21	96.27
33	80 nm	(10%) 80 nm	12.4	95.68	98.10
34	80 nm	(30%) 80 nm	10	90.47	94.77
35	80 nm	(30%) 80 nm	14.3	95.74	98.53
36	80 nm	(30%) 80 nm	10.99	96.40	98.60
37	Control	Control (u 5 nm)	9.47	95.79	99.27
38	Control	Control (u 5 nm)	8.87	94.69	98.87
39	Control	Control (u 5 nm)	9.17	96.29	97.77
40	Control	Control (5 nm)	8.09	98.25	106.10
41	Control	Control (5 nm)	7.39	97.65	105.30
42	Control	Control (5 nm)	7.89	97.05	102.70
43	Control	Control (u21 nm)	5.88	97.10	107.00

44	Control	Control (u21nm)	5.08	96.50	109.20
45	Control	Control (u21nm)	4.78	95.80	107.80
46	Control	Control (21 nm)	4.86	100.09	109.20
47	Control	Control (21 nm)	5.06	99.99	108.60
48	Control	Control (21 nm)	5.56	98.89	107.90
49	Control	Control (un80 nm)	5.77	121.38	109.17
50	Control	Control (un80 nm)	5.27	120.78	108.47
51	Control	Control (un80 nm)	4.87	119.98	107.87
52	Control	Control (80 nm)	4.28	135.23	110.37
53	Control	Control (80 nm)	3.78	134.53	109.87
54	Control	Control (80 nm)	3.28	133.83	108.97
55	Control	Control	7.5	114.15	108.30
56	Control	Control	6.9	113.75	107.60
57	Control	Control	6.3	112.95	106.80