การปรับปรุงสมบัติของเมทาคริเลต โพลีเมอร์ ทางทันตกรรมโดยใช้อลูมินา

นายพิสัยศิษฎ์ ชัยจรีนนท์

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

IMPROVED METHACRYLATE BASE POLYMER PROPERTIES IN DENTISTRY

USING ALUMINA

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A Dissertation Submitted in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy Program in Oral Biology

Faculty of Dentistry

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Thesis Title   IMPROVED METHACRYLATE BASE POLYMER

PROPERTIES IN DENTISTRY USING ALUMINA

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Field of Study   Oral Biology

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พิสัยศิษฎ์ ชัยจรีนนท์ : การปรับปรุงสมบัติของเมททาคริเลต โพลีเมอร์ ทางทันตกรรม โดยใช้อลูมินา. (IMPROVED METHACRYLATE BASE POLYMER PROPERTIES IN DENTISTRY USING ALUMINA) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ทพ. ดร. แมนสรวง อักษรนุกิจ, 121 หน้า.

วัตถุประสงค์แรกของการศึกษาเพื่อศึกษาผลของสารยึดควบคู่ชนิดต่างๆและสารละลายมีขั้วที่แตกต่างกันที่ส่งผลต่อคุณสมบัติและความแข็งแรงเฉือนของโพลีเมททิลเมททาคริเลตกับอลูมินาในสภาวะก่อนและหลังสภาวะของอุณหภูมิและความชื้นที่แตกต่างกัน และ วัตถุประสงค์ที่สองเพื่อศึกษาผลของสารยึดควบคู่ชนิดเมททอกซี่ ที่ส่งผลต่อคุณสมบัติทางกลและคุณสมบัติของการเปลี่ยนแปลงของสีของโพลีเมททิลเมททาคริเลตที่ได้รับการเสริมด้วยอลูมินา ในการศึกษาส่วนแรกได้ศึกษาค่าความแข็งแรงเฉือนระหว่างโพลีเมททิลเมททาคริเลตกับอลูมินาโดยเลือกใช้สารยึดควบคู่ 3 ชนิดคือ เอ็มพีเอส เอพีเอส และ เอเอพีเอส ร่วมกับการใช้สารละลายมีขั้วที่แตกต่างกัน 3 ชนิดคือ สารละลาย เอทานอล ไอโซโพพานอล และ โทลูอีน นำค่าความแข็งแรงเฉือน ที่ได้นำมาเคราะห์ทางสถิติชนิดการวิเคราะห์ความแปรปรวนแบบสามทางและการวิเคราะห์แบบทูกี้ ผลการศึกษาพบว่าการใช้สารยึดควบคู่ เอ็มพีเอส และ เอพีเอส ร่วมกับสารละลายเอทานอลให้ค่าแรงยึดระหว่างโพลีเมททิลเมททาคริเลตกับอลูมินาสูงที่สุดอย่างมีนัยสำคัญทางสถิติ

ในการศึกษาส่วนที่สองได้ศึกษาถึงการใช้สารยึดควบคู่ เอ็มพีเอสในความเข้มข้น 3 ระดับคือ ร้อยละ 0.1 0.2 และ 0.4 โดยน้ำหนัก และเสริมสารอัดแทรกอลูมินา ปริมาณ 3 ระดับ คือร้อยละ 10 30 และ 50 โดยน้ำหนักโดยพิจารณาผลต่อคุณสมบัติทางกลของโพลีเมททิลเมททาคริเลตที่เสริมด้วยอลูมินา กลุ่มที่ไม่เสริมเป็นกลุ่มควบคุม วิธีการทดสอบทำโดยการเตรียมรูปร่างชิ้นงานเป็นแท่งเพื่อทดสอบความแข็งแรงดัดขวาง โมดูลัสความยืดหยุ่น ความต้านทานต่อการแตกหักของชิ้นงาน และเตรียมรูปร่างของชิ้นงานเป็นแผ่นสี่เหลี่ยม เพื่อศึกษาค่าความต้านทานต่อการสึก จากนั้นนำค่าที่ได้มาวิเคราะห์ทางสถิติชนิดการวิเคราะห์ความแปรปรวนแบบสองทางและการวิเคราะห์แบบแทมเฮน ผลการศึกษาพบว่าเมื่อใช้ความเข้มข้นของสารยึดควบคู่ เอ็มพีเอส ในปริมาณร้อยละ 0.1 โดยน้ำหนัก ในการเสริมปริมาณอลูมินาร้อยละ 10 โดยน้ำหนักลงในโพลีเมททิลเมททาคริเลต ให้ค่าความแข็งแรงดัดขวางสูงที่สุด ส่วนการเสริมด้วยปริมาณอลูมินาร้อยละ 50 โดยน้ำหนักให้ค่ากำลังความทนทานต่อการหักและค่าต้านทานต่อการสึกสูงสุดอย่างมีนัยสำคัญทางสถิติ ในการศึกษาส่วนที่สามศึกษาความขุ่นและการเปลี่ยนสีของโพลีเมททิลเมททาคริเลตชนิดสีชมพูและสีใส โดยใช้ อลูมินาที่ใช้สารยึดควบคู่ชนิดเอ็มพีเอสในความเข้มข้น 3 ความเข้มข้นคือร้อยละ 0.1 0.2 และ 0.4 โดยน้ำหนัก นำค่าความขุ่นที่ได้วิเคราะห์ทางสถิติชนิดการวิเคราะห์ความแปรปรวนแบบทางเดียว จากการศึกษาพบว่า ค่าความขุ่นในกลุ่มโพลีเมททิลเมททาคริเลตสีชมพูและสีใสที่ไม่ได้เสริมด้วยอลูมินาให้ค่าความขุ่นที่ต่ำที่สุดเมื่อเทียบกับในกลุ่มที่เสริมด้วยอลูมินาอย่างมีนัยสำคัญทางสถิติ

สาขาวิชาชีววิทยาช่องปาก........................ ลายมือชื่อนิสิต..

ปีการศึกษา 2554........................ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก........................

5076454232 : MAJOR   ORAL BIOLOGY

KEYWORDS : ALUMINA / FLEXURAL PROPERTIES / SHEAR BOND STRENGTH / SILANE COUPLING AGENT / PMMA

PISAISIT CHAIJAREENONT: IMPROVED METHACRYLATE BASE POLYMER PROPERTIES IN DENTISTRY USING ALUMINA. ADVISOR: ASSOC. PROF. MANSUANG ARKSORNNUKIT, D.D.S.,Ph.D., 121 pp.

The first objective of this study was to clarify the effects of silane coupling agents and different polarity solutions on bonding between poly (methylmethacrylate) (PMMA) on alumina plate with thermocyclings challenge. The second objective was to evaluate the effects of 3-methacryloxypropyltrimethoxysilane on flexural properties, fracture toughness, wear resistance and color change of alumina reinforced poly (methylmethacrylate) (PMMA) denture base. In part 1, three silane coupling agents [3-methacryloxypropyltrimethoxysilane (MPS), 3-aminopropyltriethoxysilane (APS) and N-2 (aminoethyl) 3-aminopropyltriethoxysilane (AAPS)] and 3 different polarity solutions, 70% ethanol solution, isopropanol and toluene, were selected for silanization. The shear bond strengths were statistically compared with Tukey HSD (α=0.05). The bond strengths of PMMA on the alumina before thermocyclings were greater with MPS (15.0 MPa), APS (13.8 MPa) in ethanol solution. In part 2, the 10, 30, 50 mass% of alumina filler silanized with 0, 0.1, 0.2 and 0.4 mass% of MPS was blended with heat-polymerized PMMA. PMMA without alumina filler was served as control. Bar-shaped and square-shaped specimens were prepared for flexural properties, fracture toughness and wear resistance test, respectively (n=10). Flexural properties and fracture toughness were determined using a 3-point bending test and volume losses were measured using an in-vitro 2-body wear-testing. The flexural properties, fracture toughness and volume loss were analyzed by 2-way ANOVA and Tamhane's test (α=0.05). Flexural strength ranged from 95.1 to 115.8 MPa, fracture toughness were increase when increase amount of alumina, while volume loss ranged from 0.038 to 0.160 mm^3. In 10 mass% of alumina reinforced PMMA, the statistic analysis showed that the 0.1 mass% of silanized group was significantly higher in flexural strength and lower in volume loss than no filler and non-silanized group. In part 3, the pink and clear PMMA silanized with 0.0, 0.1, 0.2, 0.4 mass% of MPS were evaluated on the opacity and color change. The opacities value of the No filler in both of the pink and clear were significantly lower than the filler reinforced groups.

Field of Study :   Oral Biology   Student's Signature

Academic Year : 2011   Advisor's Signature

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First, I would like to express my deepest gratitude to my thesis advisor Associate Professor Dr. Mansuang Arksornnukit, who is my inspiration for working on research. He has given me valuable advice, guidance and kind assistance throughout the course. I have learnt a great deal from him and enjoyed working with him over my time at Faculty of Dentistry, Chulalongkron University. I also would like to extend my thanks to Professor Dr. Hidekazu Takahashi whom had been giving me scientific knowledge and technical supports.

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CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al	Alumina
APS	3- aminopropyl triethoxysilane
AAPS	N-2 (aminoethyl) 3-aminopropyl triethoxysilane
EDS	Element deposition analysis
ETH	Ethanol solution
FTIR	Fourier Transform Infrared Spectroscopy analysis
ISP	Isopropanol
IPN	Inter-penetrating network
MPS	Methacryloxylpropyltrimethoxysilane
PMMA	Polymethylmethacrylate
Si	Silica
TC	Thermocycling
THF	Tetrahydrofuran
TGA	Thermo gravimetric Analysis
TOL	Toluene

CHAPTER I

INTRODUCTION

Generally, poly (methylmethacrylate) (PMMA) is the most commonly used polymer material for the construction of denture bases in removable dentures. The most common problem experienced with removable dentures is the midline fractures seen in upper complete dentures [1]. Because this reason, many approaches have been advocated to strengthen PMMA. One popular modifications to improve the physical and mechanical properties is the addition of various fillers into the polymer [2,3]. Among various types of fillers, alumina powder is one of the most considerable filler types [4-6]. Previously, the addition of alumina into PMMA results in the increase of hardness [4] and thermal conductivity [5]. However, the improvement of mechanical properties by blending alumina into PMMA has not been confirmed. Alhareb and Ahmad [6] reported the increase in fracture toughness and flexural modulus but decrease in tensile strengths when adding 5% alumina into PMMA.

Silane coupling agents were advocated in improving mechanical properties of resin composites [7-9]. However, investigations on improving bond strength of alumina were mainly focused on commercial ceramic primers containing silane coupling agents [10] and the tribochemical treatment [11]. In general, there are many types of silane coupling agents formulated for the specific bonding between the fillers and the resin matrix [8,9,12]. To select the proper silane coupling agent, the solubility parameter is used to consider the dissolution of the silane coupling agent with the resin matrix, especially for thermoplastic resins [13,14]. According to the solubility parameter, 3-methacryloxypropyltrimethoxysilane (MPS), 3-aminopropyltriethoxysilane (APS) and N-2 (aminoethyl) 3-aminopropyltriethoxysilane (AAPS) are the candidates for methylmethacrylate (MMA). Different solutions were advocated in the activation of silane coupling agents silanized on silica surfaces based on their polarity; polar and non-polar [15]. In addition, the factors that affected the silanization reaction were the concentration of the silane coupling agent and the water content in the solution. The concentration of

the silane coupling agent affected the thickness of siloxane layer on the substrate [16,17]. Additionally, moisture or water content is needed for initiating hydrolysis and condensation reaction of silanes [7]. Water also affects the formation of monolayer and complete siloxane formation [18,19]. When the silane coupling agent is adsorbed on fillers, it creates bi-layer, chemisorbed and physisorbed silane layers [20]. The chemisorbed silane is absorbed on the surface via a covalent bond. The physisorbed layer is a loosely bound layer over the chemisorbed layer by the hydrogen bond and van der Waals force among silane coupling molecules. For this reason, the physical and mechanical properties created from different layers of silane would depend on the nature of deposition of silane onto filler particles; for example, amount of coupling agent, pH, rate of hydrolysis and condensation, and drying condition used in silanization. To assess good bonding between PMMA and silanized materials, the shear bond test and flexural strength test have often been used [8,21,22]. Moreover, the color stability of PMMA denture base is also a problem. This property is affected by the composition of the resin matrix, filler loading and particle size distribution [23], different types of photo-initiators [24] and percentage of the remaining $C = C$ bonds [25]. However, color stability of a material is a major concern when the amount of the filler is over mixed in PMMA. In addition, adding alumina into PMMA may affect the color stability because of the opacity of the alumina filler. Previously, the amount of the silane coupling agent, covered on the silica filler which provides optimal mechanical properties of component has previously been clarified [8,26]. However, there are no studies concerning the silanized alumina fillers on the mechanical properties. To our knowledge, the suitable amounts and types of silane coupling agents and different polarity solutions for alumina and thermocycling challenge which affect the shear bond strength, the flexural properties, wear resistance and color stability property of the alumina reinforced PMMA have not been clearly confirmed.

To cover the main objectives of this study, the experiment is mainly separated into three parts.

- The first part was to investigate the effect of various types of silane coupling agent and silanization process (solutions of different polarity) of alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

- The second part was to study on the effect of amount of sliane coupling agent of the alumina filler and amount of alumina filler on mechanical properties of methacrylate-based polymer.

- The third part was to study on the effect of amount of sliane coupling agent of the alumina filler on color change of methacrylate-based polymer.

CONCEPTUAL FRAMEWORK
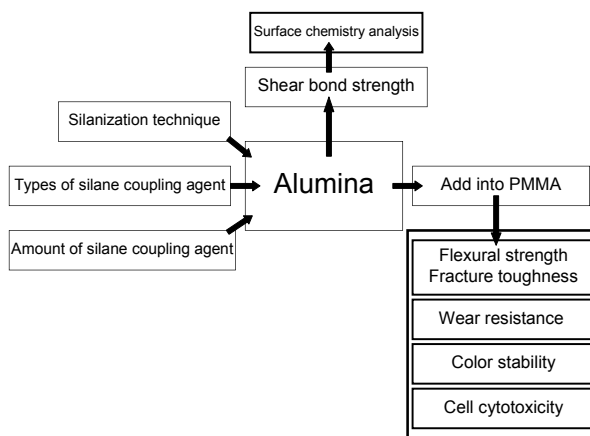
KEYWORDS

Alumina (Ai_2O_3)

PMMA

Silane coupling agent

Shear bond strength

Flexural strength

Fracture toughness

Wear resistance

Color stability

RESEARCH DESIGN

Laboratory

RESEARCH QUESTIONS

1. Whether using silanized alumina can improve methacrylate base polymer properties?
2. Whether using amount of silane coupling agent on alumina can improve methacrylate based polymer properties?

RESEARCH OBJECTIVES

The objective of part 1 was:

1. To investigate the effect of various types of silane coupling agent and silanization process (solutions of different polarity) on alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

The objectives of part 2 were:

1. To investigate the effect of amount of sliane coupling agent on the alumina filler and amount of silanized alumina filler on flexural properties of methacrylate-based polymer.
2. To investigate the effect of the amount of alumina filler on fracture toughness of methacrylate-based polymer.
3. To investigate the effect of amount of sliane coupling agent on the alumina filler and amount of alumina filler on wear resistance of methacrylate-based polymer.

The objective of part 3 was:

1. To investigate the effect of different amounts of silane coupling agent which silanized on alumina fillers reinforced in heat-polymerized PMMA on color change.

RESEARCH HYPOTHESES

The null hypothesis of part 1 was:

1. There were no differences in the shear bond strength between PMMA and the alumina plate with different silane coupling agents, silanization process (solutions of different polarity) and thermocycling challenge.

The null hypotheses of part 2 were:

1. Different amounts of alumina filler and amounts of silane coupling agents had no influence on the flexural strength and modulus of methacrylate-based polymer.

2. Different amounts of silanized alumina filler had no influence on the fracture toughness of methacrylate-based polymer.

3. Different amounts of alumina filler and amounts of silane coupling agents had no influence on the abrasive wear resistance of methacrylate-based polymer.

The null hypotheses of part 3 were:

1. Different amounts of silane coupling agent which silanized on alumina fillers reinforced in the clear heat-polymerized PMMA had no influence on color change.

2. Different amounts of silane coupling agent which silanized on alumina fillers reinforced in the pink heat-polymerized PMMA had no influence on color change.

EXPECTED BENEFITS

We anticipate that the results from this investigation would provide novel information regarding the improved mechanical properties of methacrylate-based polymer by using the alumina filler. This improved methacrylate-based material may give a promising result which could be an alternative choice for general dentists and prosthodontists in the clinical applications. This is due to the reduction of removable denture base fractures by the improvement of mechanical properties of PMMA using alumina reinforcement. We hope that the use of this modified PMMA could strengthen the denture base and this outcome would improve the long term use for partial or complete denture patients, improve patient satisfaction, and decrease overall health care costs.

CHAPTER II

REVIEW OF RELATED LITERATURE

Alumina (aluminum oxide, Al_2O_3) [27-28]

General information:

Alumina is widely distributed in nature. Alumina powder is formed by crushing crystalline alumina which is white when pure. It has a melting point at about $2,000^{\circ}C$ and a specific gravity of about 4.0. It is insoluble in water, opaque color and slightly soluble in strong acids and alkalines. Alumina occurs in two crystalline forms (alpha and gamma). Alpha alumina is composed of colorless hexagonal crystals which is the only stable alumina phase at all temperatures. On the other hand, gamma alumina is composed of minute colorless cubic crystals with a specific gravity of about 3.6, which can be transformed to the alpha form at high temperatures. Additionally, alumina powder is the major component of bauxite (sedimentary rock that is an aluminum ore) and occurs in an almost pure form as corundum (crystalline form of aluminum oxide (Al_2O_3) with traces of iron, titanium and chromium). Alumina is commercially important.

How to use alumina:

In industry, a major use of alumina is in the production of aluminum metal. It is also used for abrasives; corundum and emery which are widely used in preparation for alumina abrasives. Many types of sandpaper use aluminium oxide crystals. Alumina is also used in ceramics called alumina ceramics. Alumina ceramic contains at least 80% of aluminum oxide (Al_2O_3). Small amounts of silica (SiO_2), magnesia (MgO) and zirconia (ZrO_2) may be added to alumina ceramics. Addition of zirconia to alumina ceramic results in a considerable increase in fracture toughness. Moreover, alumina has a strong ionic bonding, which affects its properties as follows;

- High flexural strength and hardness

- High wear resistance

- High resistance to chemical attacks of strong acids and alkali even at high temperatures

- High stiffness

- Excellent insulating properties

- Low coefficient of thermal expansion

- Good fracture toughness

- Good thermal conductivity

- Good biocompatibility

Aluminum ceramics are manufactured by the many technologies: uniaxial (die) pressing, isostatic pressing, injection molding, extrusion and slip casting. Moreover, aluminum ceramics are widely used in electronics, electrical engineering, metallurgical processes, chemical technologies, medical technologies, mechanical engineering, and military equipment.

In medicine, alumina is used in articulating surfaces of artificial joints. This is due to its ability to be polished to a high luster and its excellent wear resistance. Alumina is often used for surfaces subjected to wear in joint replacement prostheses. Such applications include femoral heads for hip replacements and wear plates in knee replacements. In hip replacements, the wear rate for alumina on ultra high molecular weight polyethylene has been reported to be as much as 20 times less than that for metal on ultra high molecular weight polyethylene, making this combination far superior and producing less tribological debris. This debris could lead to complications in surrounding tissues, so keeping debris to a minimum is advantageous.

Alumina has also been used in dental applications such as dental porcelains, filler in dental polymers, dental abrasive materials, coating materials, and dental instruments.

<u>Effect on cell biology:</u> [29-31]

The advantage of alumina in the cell biology was used in the medical field, for example, porous alumina used as a scaffold for bone formation in the area that bone has been removed such as cancer. The porous nature of these implants will allow new bone to grow into the pores. Additionally, the effect of alumina in the bone remodeling was also investigated. From the previous study [29] which studied the effects of polyethylene and alumina particles on IL-6 expression of human osteoblastic cells showed the result that at high dose, the alumina particles had a lower capacity than the polyethylene particles to stimulate IL-6 production in human osteoblasts which resulting in the more cellular proliferation, induce osteoclast formation and stimulate osteoclasts to resorb bone. Therefore, the stimulation from polyethylene appears to be stronger than that from alumina particles. However, the grain size of alumina particle might affected the bone cell response, comparing between the 1 μm and 12 μm grain size of alumina filler, the result showed that the proliferation of OPC1 and cell attachment growth and differentiation of 12 μm grain size alumina particle were better than those of 1 μm grain size samples. In addition, a broader distribution of bigger grain size may have provided more favorable for OPC1 cell-activity. These results were not consistence with the effect on human lung epithelial cells [30]. From the previous study, at the levels of 5–25 μg/mL dose range, the size of aluminum oxide particle did not influence in cytotoxicity of human lung epithelial cells. However, comparing among Al_2O_3, negative control (TiO_2) and positive control (CeO_2), the cytotoxicity of both Al_2O_3 nanoparticles were higher than negative control TiO_2 nanoparticles but lower than positive control CeO_2 nanoparticles. Determining the depolarization, the 13 nm Al_2O_3 nanoparticles resulted in more significant depolarization than the 30nm Al_2O_3 particles. The discussion of this study claimed that the smaller particles of Al_2O_3 particles cause greater toxicity because of their relatively larger specific surface area. Additionally, the reason of that the both Al_2O_3 particles showed similar cytotoxicity might be due to their similar aggregation size in cell culture medium [31].

Silane Coupling Agents [8, 16, 17, 19, 32-34]

Silane coupling agents are silicon-based chemicals that contain two types of reactivity – inorganic and organic – in the same molecule. A typical general structure is $(RO)_3SiCX-Y$, where RO is a hydrolyzed group, such as methoxy, ethoxy, or acetoxy, and X is the carbon backbone and Y is an organofunctional group, such as amino, methacryloxy, epoxy, etc. A silane coupling agent acts at the interface between inorganic and organic substrates and provides the covalent bond between two different materials (Figure 1).
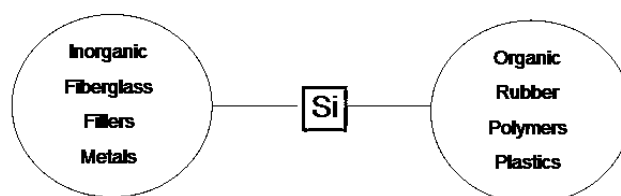
Figure 1 Schematic of the silane coupling mechanism.

When polymers are reinforced with inorganic fillers, the interface between the polymer and the inorganic substrate is involved in a reaction of physical and chemical factors. These factors are related to adhesion, physical strength, and coefficient of thermal expansion. The destructive phenomenon, which affects adhesion, is the absorption of water to the hydrophilic surface of inorganic fillers. Water molecule attacks the interface, and breaks the bond between the polymer and fillers reinforcement. With a coupling agent, it creates a water-resistant bond at the interface between inorganic fillers and organic materials resulting in a good adhesion. The coupling agent provides a stable bond between two bonding surfaces. In composites, an increase in flexural strength is achieved by the use of a proper silane coupling agent. Silane coupling agents also increase the bond strength of coatings and adhesives. Other benefits of silane coupling agents in improving the properties of composite are increase surface wetability of inorganic substrates, lower viscosities during compounding, smoother

surfaces of composites, less catalyst inhibition of thermoset composites, clearer reinforced plastics

Reaction of the Silane Bond to the Inorganic Substrate

Silane coupling agents that contain three inorganic reactive groups on silicon (usually methoxy, ethoxy or acetoxy) can bond well to metal oxide on inorganic substrates, especially if the substrate contains silicon, aluminum or a heavy metal in its structure. The alkoxy groups on silicon are hydrolyzed and form silanols, either through the addition of water or from residual water on the inorganic surface. Then, silanols coordinate with metal oxide on the inorganic surface to form a siloxane bond and water is eliminated (Figures 2 and 3). Silane molecules also react with each other to form a structure of a bound silane coupling agent on the surface which is a tight siloxane network closed to the inorganic surface, and becomes more diffuse away from the surface.
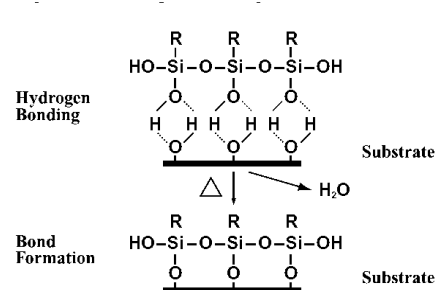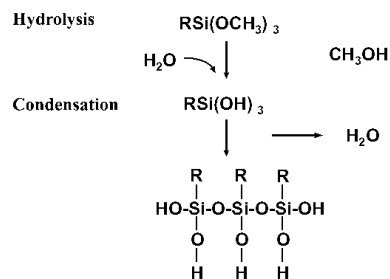
Figure 2 Hydrolysis of alkoxysilanes.   Figure 3 Bonding to an inorganic surface.

The reactivity of a polymer should match the reactivity of the silane. With polymers, bonding through a silane coupling agent can be explained by inter-diffusion and inter-penetrating network (IPN) formation in the interphase area (Figure 4). To create an appropriate IPN formation, it is important that silane and resin are compatible. One method is to match the chemical characteristics of the two materials. This helps improve chances of forming a good composite with optimum properties.

Diffuse Inter*phase*

Si--O--Si--

Si--O--Si--

Silica

Si--O--Si--

Si--O--Si--

◯ Coupling Agent ◯ Polymer
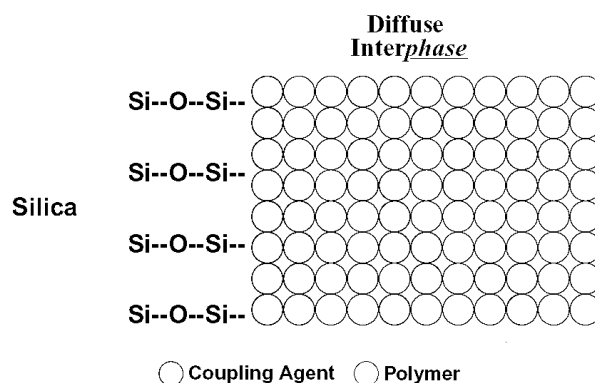
Figure 4 Schematic of the inter-penetrating network (IPN) bonding mechanism.

      The choice of silane should be compatible with the properties of the polymer such as chemical reactivity, solubility characteristics, structural characteristics and thermal stability of the organosilane in the polymer structure. Moreover, it provides modified characteristics to inorganic surfaces, including hydrophobicity, organic compatibility and lower surface energy. Recommended application of silane coupling agents with various polymer types according to the manufacturer's information (Shin-Etsu Chemical, Tokyo, Japan) are provided in Table 1.
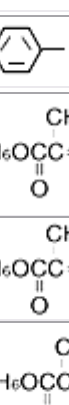
Table 1. Silane coupling agent recommendations for various polymer-matching
organo-reactivity to polymer type.

Organic Reactivity	Application (suitable polymers)
Amino	Acrylic, Nylon, Epoxy, Phenolics, PVC, Urethanes, Melamines, Nitrile Rubber
Benzylamino	Epoxies for PCBs, Polyolefins, All Polymer Types
Chloropropyl	Urethanes, Epoxy, Nylon, Phenolics, Polyolefins
Disulfido	Organic Rubber
Epoxy	Epoxy, PBT, Urethanes, Acrylics, Polysulfides
Epoxy/Melamine	Epoxy, Urethane, Phenolic, PEEK, Polyester
Mercapto	Organic Rubber
Methacrylate	Unsaturated Polyesters, Acrylics, EVA, Polyolefin
Tetrasulfido	Organic Rubber
Ureido	Asphaltic Binders, Nylon, Phenolics; Urethane
Vinyl	Graft to Polyethylene for Moisture Crosslinking, EPDM Rubber, SBR, Polyolefin
Vinyl-benzyl-amino	Epoxies for PCBs, Polyolefins, All Polymer Types

A correlation between the chemistry and structural characteristics of the silane coupling agent and the chemistry and structural characteristics of the polymer according to the manufacturer's information (Shin-Etsu Chemical, Tokyo, Japan) was shown in Table 2.

Table 2. Chemistry and structural characteristics of silane coupling agent.

Functional group	Chemical name	Structural formula
Vinyl	Vinyltrichlorosilane	$Cl_3SiCH{=}CH_2$
	Vinyltrimethoxysilane	$(CH_3O)_3SiCH{=}CH_2$
	Vinyltriethoxysilane	$(C_2H_5O)_3SiCH{=}CH_2$
Epoxy	2-(3,4 epoxycyclohexyl) ethyltrimethoxysilane	$(CH_3O)_3SiC_2H_4-$ (epoxycyclohexyl ring)
	3-glycidoxypropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6OCH_2CH{-}CH_2$ (epoxide)
	3-glycidoxypropylmethyldiethoxysilane	CH_3; $(C_2H_5O)_2SiC_3H_6OCH_2CH{-}CH_2$ (epoxide)
	3-glycidoxypropyltriethoxysilane	$(C_2H_5O)_3SiC_3H_6OCH_2CH{-}CH_2$ (epoxide)
Styryl	p-Styryltrimethoxysilane	$(CH_3O)_3Si-$ (benzene ring) $-CH{=}CH_2$
Methacryloxy	3-methacryloxypropylmethyldimethoxysilane	CH_3 CH_3; $(CH_3O)_2SiC_3H_6OCC{=}CH_2$; $\overset{\parallel}{O}$
	3-methacryloxypropyltrimethoxysilane	CH_3; $(CH_3O)_3SiC_3H_6OCC{=}CH_2$; $\overset{\parallel}{O}$
	3-methacryloxypropylmethyldiethoxysilane	CH_3 CH_3; $(C_2H_5O)_2SiC_3H_6OCC{=}CH_2$; $\overset{\parallel}{O}$
	3-methacryloxypropyltriethoxysilane	CH_3; $(C_2H_5O)_3SiC_3H_6OCC{=}CH_2$; $\overset{\parallel}{O}$

Acryloxy	3-acryloxypropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6OCCH=CH_2$ with $\|$ O below
Amino	N-2(aminoethyl)-3-aminopropylmethyldimethoxysilane	CH_3 above $(CH_3O)_2SiC_3H_6NHC_2H_4NH_2$
	N-2(aminoethyl)-3-aminopropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6NHC_2H_4NH_2$
	N-2-(aminoethyl)-3-aminopropyltriethoxysilane	$(C_2H_5O)_3SiC_3H_6NHC_2H_4NH_2$
	3-aminopropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6NH_2$
	3-aminopropyltriethoxysilane	$(C_2H_5O)_3SiC_3H_6NH_2$
	3-triethoxysilyl-N-(1,3-dimethyl-butyliden)propylamine and partially hydrolyzed substances	$(C_2H_5O)_3SiC_3H_6N=C$ with branches C_4H_9 and CH_3
Amino	N-phenyl-3-aminopropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6NH$ —⬡
	N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane hydrochloride	Methanol solution, Active ingredients: 40%
	Proprietary aminosilane	Methanol solution, Active ingredients: 50%
Ureid	3-ureidopropyltriethoxysilane	$(C_2H_5O)_3SiC_3H_6NHCNH_2$ with $\|$ O below; Methanol solution, Active ingredients: 50%
Chloropropyl	3-chloropropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6Cl$
Mercapto	3-mercaptopropylmethyldimethoxysilane	CH_3 above $(CH_3O)_2SiC_3H_6SH$
	3-mercaptopropyltrimethoxysilane	$(CH_3O)_3SiC_3H_6SH$
Polysulfide	Bis(triethoxysilylpropyl)tetrasulfide	$(C_2H_5O)_3SiC_3H_6S_4C_3H_6Si(OC_2H_5)_3$
Isocyanate	3-isocyanatepropyltriethoxysilane	$(C_2H_5O)_3SiC_3H_6N=C=O$

<u>Calculating the Required Amount of Silane</u> [17]

The silicone molecule is preferably attached to the surface of the inorganic material as a primer to form a monolayer. Applying the silane as a primer will produce optimum coupling results between the substrate and the resin. When used as a primer, the required amount of silane can be calculated by the following equation:

$$\text{Amount of silane (g)} \quad = \quad \frac{\text{Amount of filler (g) x Surface area (m}^2\text{/g)}}{\text{Minimum coating area of silane coupling agent (m}^2\text{/g)}}$$

The actual values may deviate from the calculated value depending on the surface condition of the filler or the silane treating process. There are many studies describing the use of silane coupling agents with dental materials.

Rathke et al. (2009)[35] investigated the effect of different mechanical and adhesive treatments on the bond strength between the pre-existing composite and the repaired composite using two aging times of the composite to be repaired. The authors concluded that the adhesive treatment of the mechanically roughened composite is essential for achieving acceptable bond strengths. The use of silica-coated particles for sandblasting, followed by a silane coupling application had no advantage over common bonding systems.

 Shimizu et al. (2009) [36] evaluated the effect of the surface preparation on the maximum fracture load value of a highly filled gingival shade composite resin bonded to a denture base resin. The authors concluded that tribochemical silica coating and the application of dichloromethane after applying the silane coupling agent were the effective surface preparations for the bonding of a highly filled composite resin to a denture base resin; however, the bond durability of these treatments may be insufficient.

Sideridou et al. (2009) [26] evaluated the effect of the amount of 3-methacryloxypropyl-trimethoxysilane coupling agent on some physical–mechanical properties of an experimental resin composite. The authors concluded that no significant statistical difference existed between the flexural strength and flexural modulus of

composites with different silane contents. However, the amount of silane used for the silanization of silica particles had an effect on the orientation of silane molecules relative to the silica surface. This seemed to affect the dynamic mechanical properties of composites.

Matinlinna et al. (2008) [37] studied four experimental blends of an organo-functional silane monomer with a non-functional cross-linking silane monomer (a novel silane system) and evaluated them as adhesion promoters in an experiment, in which a resin-composite cement was bonded to silica-coated titanium. The authors concluded that a novel silane system with an optimal concentration of the cross-linking silane produce significantly higher shear bond strength between silica-coated titanium and resin-composite cement compared to a pre-activated silane product.

Karabela et al. (2008) [38] studied adsorption characteristics of water or ethanol/water solution (75/25 vol%) of nanocomposites consisting of a Bis-GMA/TEGDMA (50/50, wt/wt) matrix and silica nanoparticles as filler, silanized with various silanes. The authors concluded that the silane structure used for the silanization of nanosilica affected the adsorption behavior of water or ethanol/water solution ($37^{O}C$) by composites. The composite containing a silane with the hydrophilic urethane group showed the highest amount of absorbed water. The composite with a silane which did not contain a methacrylate moiety and could not react with dimethacrylate monomers showed the highest solubility both in water and ethanol/water. In all composites, the amount of absorbed ethanol/water solution was much higher than that of water.

Technique of silanization

Silanes can be classified into 2 types as single-phase pre-activated solutions and two-component systems that have to be mixed in order to initiate the hydrolysis reaction. Pre-activated silane solutions are composed of three ingredients: [39]

1. silane coupling agent
2. acid component
3. solvent

In addition, the silanization techniques can be separated according to the polarity of solution (polar and non-polar) [15]. There are several studies evaluate different techniques of silanization.

Hooshmanda et al. (2004) [39] prepared a silane solution by mixing 2.5% γ-MPS with 2.5% acetic acid, and 95% ethanol by volume and , then, kept for different periods of time. The authors found that the chemical stability and bonding efficacy of pre-activated silane solutions would be detrimental over time.

Oliveira et al. (2005) [40] prepared a silane solution by two different methods, using a non-polar and a polar solvent. A 10 wt% γ-methacryloxypropyltrimethoxy- silane (γ–MPS) was dissolved in a 95/5 (V/V) methanol/water solution for the polar method and 2 wt% n-propylamine in cyclohexane solution was used for the non-polar method. This study evaluated the effect of silanization technique on Bonelike$^{@}$/PLGA hybrid materials for bone regeneration. The authors concluded that silanization of hydroxyapatite (HA) and bonelike material was successfully obtained by using γ-MPS as a coupling agent.

Santos et al. (2001) [41] treated surface of HA powder with γ–MPS by two methods (non-polar and polar). The non-polar method was prepared by dissolving 10 wt% of γ–MPS in cyclohexane with 2 wt% of n-propylamine. For the polar method, 10 wt% of γ–MPS was dissolved in a 95/5 (V/V) methanol/water solution. The authors found that the incorporation of HA filler into the Bis GMA base resin had an enhancing effect on the flexural strength and Young's modulus of the base resin. The mechanical properties of the filled resin were not affected by the surface treatment of the HAp, but filler loading was found to have a significant effect on Young's modulus.

Loch CL et al. (2007) [14] prepared silane adhesion-promoting mixture (SAPM) by mixing toluene (non-polar) with (3-glyci-doxypropyl) trimethoxysilane (γ-GPS) and methylvinylsiloxanol (MVS). This solution was prepared for the coating on thin polymer films. The authors found that sum frequency generation studies on polymer/ γ-GPS and polymer/silane adhesion-promoting mixture (SAPM) interfaces revealed that silane molecules diffused through PMMA and dissolved polystyrene. Additionally, the diffusion time of γ-GPS through d-PMMA was longer at the polymer/SAPM interface than at the polymer/neat silane interface.

Yoshino N et al. (1995) [42] studied modification of the glass surface using silane coupling agents, and also investigated oxidation resistance of the modified glass surface. The silane compounds solutions were prepared by dissolving silane coupling agents in benzene, toluene and hexane. The authors concluded that silane coupling agents showed a high degree of surface modification.

Aboudzadeh et al. (2007) [43] prepared hydrolyzed silane in a dilute aqueous solution by adding silanes to a mixture of 70:30 ethanol and distilled water. The pH of the solution was adjusted to 4.5–5.5 by adding a few droplets of acetic acid. For this technique, the SiOR groups of silanes were transformed to active the SiOH groups. The authors from this study concluded that the effect of epoxy silane in increasing adhesion strength of flame-treated PP surfaces was higher than the aminosilane.

Kasraei SH et al. (2008) [44] evaluated the effect of the solvent type of silane solution on microtensile bond strength of fiber posts to composite resin cores after the application of 24% hydrogen peroxide. Silane solutions were prepared by incorporating 1 wt% of γ-methacryloxypropyltrimethoxy-silane (γ-MPS) into the ethanol and acetone based solvents. The authors concluded the type of solvent in silane solution had no effect on microtensile bond strength between fiber posts and composite resin cores after the application of 24% hydrogen peroxide.

From the above-mentioned literature, it seems that the application of silane is still controversial and in conclusive. To date, there are no information and studies which compare the effect of various types of silane coupling agents and silanization techniques (different polarity of solutions) on alumina.

Fracture Mechanics

The average masticatory force has been reported to vary between 11 and 150 N, whereas force peaks were reported to be 200 N in the anterior, 350 N in the posterior and 1000 N in patient with parafunctional habits [45]. Thus, it is important to evaluate the mechanical properties of materials *in vitro* which might be advantage in clinical application. For example, strength is defined as the ultimate stress that is necessary to

cause fracture or plastic deformation and is strongly affected by the size of flaws and defects present on the surface of a tested material. Flexural strength and fracture toughness characterize the responses of materials, such as brittle dental ceramics, to loading forces and crack propagation [46].

Mechanical properties tests used in this study for the improvement of methacrylate-based polymer properties in dentistry using alumina

Fracture Toughness [47]

Fracture toughness is an indication of the amount of stress required to propagate a preexisting flaw. This parameter is a very important material property because the occurrence of flaws is not completely avoidable in the processing, fabrication, or service of a material. Flaws may appear as cracks, voids, weld defects or design discontinuities. Since engineers can never be totally sure that a material is flaw free, it is common to assume that a flaw will be presented in some number of components and to use the linear elastic fracture mechanics approach to design critical components. This approach uses the flaw size and features, component geometry, loading conditions, and the material property, which is called fracture toughness to evaluate the ability of a component containing a flaw to resist fracture. The stress-intensity factor (K) is used to determine the fracture toughness of most materials. A Roman numeral subscript indicates the mode of fracture and the three modes of fracture are illustrated in Figure 5.
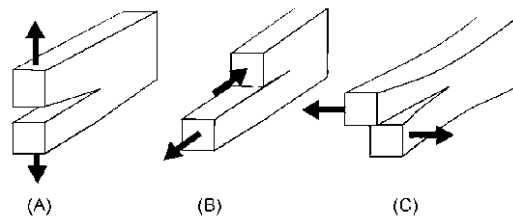
Figure 5 Schematics of three different failure modes (A) Represents mode-I (tensile force), (B) represents mode-II (shear force) and (C) represents mode-III (torsional force)

Mode I fracture (tension mode) is the condition in which the crack plane is normal to the direction of the largest tensile loading. This is the most commonly encountered mode and, the most widely used fracture toughness test configurations are the single edge notch bend (SENB or three-point bend) test.

The test for Mode II fracture (shear mode) and Mode III fracture (torsional mode) is also frequently conducted; however, a specific test method has not yet to be standardized by the American Society for Testing and Materials (ASTM). The most common method is to simply load specimens in the three-point bending test. The shear stress at the mid-plane (center) of the specimen initiates the desired Mode II sliding failure (crack propagation) at the end of the insertion. This test method is commonly referred to be the End-Notched Flexure (ENF) test. Mode II and mode III are stressed intensity factors, which are the fracture modes when the loading direction is parallel to the crack plane. These conditions rarely occur in metals and are not used for ceramics.
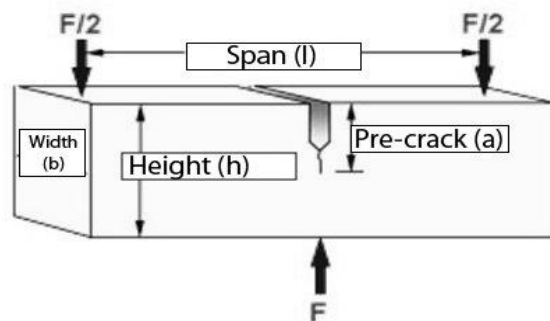
Figure 6 Schematics of single edge notch bend or three-point bend test

The accumulated data were used to determine the fracture toughness (K_{Ic}) in MPa-m$^{1/2}$. Fracture toughness (K_{Ic}) was calculated according to the formula: [48, 49]

$$K_{max} = f\ P_{max}l_t\ /\ (b_t h_t^{3/2}) \times \sqrt{10^{-3}} \qquad MPa \cdot m^{1/2}$$

where,

f is a geometrical function dependent on x

$f(x) = 3x^{1/2}[1.99-x(1-x)(2.15-3.95x+2.7x^2)/[2(1+2x)(1-x)^{3/2}]$

and

$x = a/h_t$

P_{max} is the maximum load exerted on the specimen, in newtons;

Height $h_t = 8.0 \pm 0.2$ mm

Width $b_t = 4.0 \pm 0.2$ mm

Pre-crack $a = 3.0 \pm 0.2$ mm

Span $l_t = 32.0 \pm 0.1$ mm

Flexural strength

Flexural strength is a mechanical parameter for a brittle material, which is defined as the ability of a material to resist deformation under load. Resistance of a material to functional loads which is a mechanical factor must be considered when choosing a material for clinical use. The transverse bending test is the most frequently test. In this test, the rod specimen would either be a circular or rectangular cross section, which is bent until fracture using a three point flexural technique. The flexural strength represents the highest stress experienced within the material at its moment of rupture. This parameter is a combination of compressive, tensile, and shears strengths. As tensile and compressive strengths increase, the force required to fracture the material also increases. For rectangular shape, flexural strength (F) of the 3-point bending test is calculated according to the formula: [50]

$$F = 3\,FL\,/\,2BH^2$$

Where   F is the maximum load (N) in the load - displacement curve.

L the support span length,

B the width of the specimen,

H the thickness of the specimen.

In clinical situation, most denture fractures occur intraorally during function, primarily because of resin fatigue [51, 52]. The denture base resin is subjected to resist various stresses during function such as compressive, tensile, and sheer stresses. One of the most common causes of denture fracture is fatigue [52].

Wear resistance test

Wear resistance is one of the most important physical properties of PMMA that is used in removable partial or complete dentures. Cross-linked acrylic denture bases have been developed to increase the resistance to crazes and wear by various polymer technologies including blended polymer and interpenetrating polymer networks (IPN). [53,54] Causes of wear on denture bases are more often related to different brushing techniques such as using an incorrect toothbrush (abrasion wear), the action of the toothbrush, incorrect toothpaste and types of food patients eat (attrition of food bolus). The main elements of *"wear"* can be categorized into three parts: first body, second body, and interfacial elements (third body). These may be explained as follows: [54]

First body: The body being worn.

Second body: Any counterface body the wear of which is not of immediate concern, in motion relative to the first body and in direct or indirect contact such that forces can be transmitted to the first body. The second body is often the main cause of the wear to the first body.

Interfacial elements (third body): Any materials (whether autogenously generated or foreign matter) and other special conditions which might be presented at the interface between the first and second bodies. Examples are wear debris, lubricants, entrained solid particles and reactive chemicals.

Shear bond strength

Shear bond strength is a measurement of how well one material bonds to another. It places the bond interface in shear. The present invention provides an apparatus and a method to apply a load to an adherent, which is bonded to a substrate, to allow an accurate measurement of the bond between an adherent and substrate. This is accomplished by positioning a crosshead at the base of the adherent and applying a load, which is parallel to the surface of the substrate against the base of the adherent. The strength of the bond is the force per unit area required to shear the adherent from the substrate. The accuracy of the measurement is enhanced by minimizing the surface area of the material that is in contact with the substrate and by ensuring that the adherent is not fractured during testing. Fracturing and deformation of the adherent is limited by using a notch to test with rather than a straight chisel. There are many versions of the test that utilize an anvil to load the side of a cylinder of material that is bonded at one of its ends to a substrate material. The present invention is configured to load the adherent such that the strength of the bond may be measured accurately. Typical measurement units are in Mega Pascals (MPa).

Yoshida (1999) [55] studied the effect of MMA–PMMA resin polymerization initiators on bond strengths of two adhesive metal primers by evaluating the shear bond strengths of resins to silver–palladium–copper–gold (Ag–Pd–Cu–Au) alloy. The authors concluded that no significant differences in bond strength between the three types of resins with or without thermal cycling when Metal Primer II was used. Metal Primer II was more effective for enhancing the bond strength and the bond strength was not affected by thermocycling, in contrast to V-Primer.

Guler (2005) [56] studied shear bond strengths of resin composite to porcelain according to the surface treatment. The authors concluded that bond strengths were significantly different. The highest to the lowest bond strength was observed in the sandblasting with 50-µm Al_2O_3 + acid etching + silane group (12.34 MPa), acid etching + silane group (11.97 MPa) and the silane group (4.09 MPa), respectively.

Stangeli (1987) [57] studied the bond strength of composite resin to porcelain by varying porcelain manipulation and bonding procedures. The following conditions: (a) no etching, (b) etched with 52% (w/w) hydrofluoric acid for 90 seconds, and (c) etched with 20% (w/w) hydrofluoric acid for 2.5, 5, 10, and 20 minutes were used. The results indicated a significant difference in shear bond strength for the three bonding groups, depending on the porcelain surface condition. For the un-etched samples, significant differences in bond strength were obtained for all three bonding conditions. However, for the etched group, there were no differences between the silane and silane-with dentin- adhesive groups. Porcelain etching significantly increased bond strength across all three bonding methods and was the main contributor to the obtained values.

The effects of bonding between two materials are depending on solubility parameter. The Hildebrand parameter (δ) provides a numerical estimate of the degree of interactions between materials and can be a good indication of solubility, particularly for non polar materials such as many polymers. Materials with similar solubility parameters will be able to interact with each other, resulting in salvation, miscibility or swelling. The Hildebrand solubility parameter is the square root of the cohesive energy density. The cohesive energy density is the amount of energy needed to completely remove unit volume of molecules from their neighbors to infinite separate (an ideal gas), which is equal to the heat of vaporization divided by molar volume. In order for material to dissolve, these same interactions need to be overcome as the molecules separated from each other and surrounded by solvent [58].

CIELAB

CIE *L*a*b* (CIELAB) is the most complete color space specified by the CIE in 1976. Values from the CIE color system can be calculated to find the difference of color between the samples compared to the standard sample. The total color change obtained is calculated for each specimen using the equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where ΔL^*, Δa^* and Δb^* are the differences in the respective values of the two points of color coordinate which will be compared. In dentistry, visual perceptible color difference is set at $\Delta E > 1$ while clinical accepted of color match is set at $\Delta E < 3.3$ [59, 60].

Review related literatures:

According to previous studies, many attempts were made trying to improve mechanical properties of PMMA. One of the popular modifications is the addition of various fillers into the polymer. Various types of fillers were added into PMMA for example Al_2O_3, ZrO_2, and SiO_2. The flexural strength of PMMA added with different ratios of Al_2O_3/ ZrO_2 were compared, and the results showed that additional with 5 wt% of 80/20; Al_2O_3/ZrO_2 could improve the flexural modulus, tensile strength and tensile modulus of PMMA. Additionally, the addition of more Al_2O_3 than ZrO_2 into PMMA resulted in a slight increase of the flexural modulus [61]. This result was supported by another study which suggested that Al_2O_3 fillers had potential to provide an increase in the flexural strength and thermal diffusivity of denture bases. Incorporating Al_2O_3 powder from 5% to 20% by weight into a conventional heat-polymerized denture base resin resulted in an increase in both flexural strength and thermal diffusivity [5]. However, the alumina fillers used in this study were not silanized. Another study attempted to modify the properties of the bone cement by adding γ-MPS silanized on the alumina filler, the results showed that silanized alumina reinforced with PMMA reduced the production of wear particle and debris. Unfortunately, the high concentration of silanized alumina filler

could improve the compressive strength and modulus but could not be processed due to the lack of liquid monomer to wet the filler surface and dissolve the PMMA beads [62]. This previous study, however, did not evaluate the important mechanical properties such as fracture toughness or the bond strength between the alumina filler and the PMMA matrix.

In order to use a silane coupling agent, many factors that affected the rate of hydrolysis reaction such as silane concentration, solution [63], temperature, water content, nature of a silane, and type of substrate should be considered [64]. For the condensation reaction, the self condensation reaction can be controlled by using fresh solution, alcohol solvents, dilution, and optimal pH range [63]. Additionally, the conditions which promote the hydrolysis of alkoxysilanes also promote condensation of silanols [65]. Moreover, the siloxane layer thickness is affected by the concentration of the silane solutions. If the substrate is aluminum, -Si-O-Al- bond seems to be poor hydrolytic stability [9]. There are two types of silane used in dentistry; methoxysilane and aminosilane. The most commonly used methoxysilane is a monofunctional γ-methacryloxypropyltrimethoxysilane (or 3-trimethoxysilylpropylmethacrylate (MPS). This silane is usually diluted, often less than 2 wt% in water-ethanol solution, with its pH of 4 to 5, adjusted by acetic acid [9]. MPS was synthesized and widely tested, first with the glass fiber then; it became an interesting choice for coupling porcelain teeth to acrylic denture resins [9]. Regarding the structure of silane, the most effective structure of silane for adhesion are the short backbone body structure and hydrolysable methoxy groups for the organo-functional part [66]. This is in contrast with another which claimed that the weak point of methoxysilane in propanal solution bonded to alumina was unstable over time in water [10]. On the other hand, aminosilanes are known using of all four active groups: three methoxy groups and amine for forming hydrogen bonding with hydroxyl. At concentrations lower than 0.2%, the aminosilane exists as a monomeric silane triol [65]. The orientation of physisorbed silane of aminosilane can change from primary a methoxy group at low concentration to an amine bonded group at a higher concentration. Additionally, the additional treatment with water could eliminate improper

orientation of aminosilanes, but did not succeed in forming a Si-O-Si bond with the surface [19]. When comparing between methoxysilane and aminosilane, the rates of hydrolysis of the alkoxy groups are generally related to their steric bulk. For this reason, the rate of hydrolysis of methoxysilane (CH_3O) is higher than that of aminosilane (C_2H_5O, t-C_4H_9O) [65]. With the exception of aminosilanes, most silanes are employed in surface treatment applications under acid-catalyzed conditions [65].

The effectiveness of the coupling action with silanes depends on several criteria as follows; [63]

1. The good mechanical dispersion of the silane into the coating will assure uniform coupling and the best efficiency.

2. The solubility parameter and reactivities of the polymer and silane must be compatible. There should be no reactions occurred in storage. Matched solubility is necessary for silane interpenetration into the polymer. [67]

3. Silane, as additives in filled systems, in storage will migrate to the inorganic surfaces of fillers. Some excess silane should be added so that it could be adsorbed onto the mineral surface of the fillers and to replace silane which fails to migrate through the polymer to the coating/substrate surface.

4. Hydrolysis of silane triol by water must occur to render active silane for coupling. Proper moisture conditioning of filler or addition of extra water will assure the silane hydrolyzation and coupling process.

The solution in silanization process is an important factor to consider. A previous study claimed that the most straight-forward method to silanize a surface with a silane was from an alcohol solution. A two percent silane solution can be prepared in the methanol, ethanol, and isopropanol. Additionally, sufficient water hydrolysis in the reaction may be available from atmospheric moisture, or on the substrate surface. The water in the silanization process might play the important role in affecting the high ordered monolayer formation [63]. In general, there are two models of silanization. The

first model is the forming of a continuous growth of a liquid-like disordered film then it further improves to a well-ordered monolayer with an increase in the total coverage. The second model is the formation of close-packed islands from the beginning. Initially, the islands are separated by uncovered regions and grow by lateral polymerization until a full coverage is reached. The water content in the silane solution is important because it affects the mechanism of layer formation changing from continuous growing at low moisture to the island growth at the higher water content. The increasing in water content causes silane polymerization to initiate in solution and later deposit on the surface [64]. For methoxysilane, silanization in dry conditions cannot produce monolayer films with the highest density due to the steric hindrance. The sparse monolayer, where only a single methoxy group per silane reacted with the surface hydroxyl and the other two methoxy groups remained unreacted, is formed. If water is present in the solution, hydrolysis of some methoxy groups allows their vertical polymerization in the solution or start polymerization from the immobilized surface of silane [19].

The other factor affected the usage of PMMA is the color change which concerns the patients. The factors which influence this property are from extrinsic and intrinsic factors. The extrinsic influences are from attained food, colored mouth rinses, intensity and duration of the polymerization of PMMA [68, 69], exposure to environmental factors, heat, water [70] or food colorants [71-73]. On the other hand, the endogenous discoloration can be found in ultraviolet (UV) irradiation and thermal energy. The UV light can induce physico-chemical reactions in the polymer by degradation the polymer molecules which may change their properties. The factor which plays decisive roles in the extent of discoloration is the polymeric structure and surface roughness caused by various substances. Moreover, color change is also affected by the composition of the resin matrix, filler loading and particle size distribution [9], type of photo-initiator [74] and percentage of the remaining $C = C$ bonds [25]. However, color change of materials is a major problem if the amount of fillers is over mixed in PMMA.

To our knowledge, the suitable amount and type of silane coupling agents and different polar solutions for alumina and thermocycling challenge effects on the mechanical properties and color change of the alumina reinforced PMMA have not been clearly confirmed. For the silanization process, the solution might play the important role. Various types of solutions have been suggested. From previous studies, ethanol, isopropanol and toluene are often used based on their polarity. However, these studies have focused on silanization for silica, but not for alumina. Additionally, there have been no previous studies which conclude the effect of the silanization process and amount of silane on bonding between alumina and resin matrix. Moreover, the information on what kind of suitable silane coupling agent for alumina, the amount of silane and the solvents for silanization have not been confirmed. The main objectives of this study are to find the suitable silane coupling agent, amounts of silane coupling agent and silanization techniques for alumina with the aim to use this silanized alumina to improve the properties of methacrylate base polymer in dentistry.

To cover the main objectives of this study, the experiments are mainly separated into 3 parts.

1. The first part was to investigate the effect of various types of silane coupling agent and silanization process (solutions of different polarity) of alumina plate and thermocycling challenge on the bond strength to methacrylate-based polymer.

2. The second part was to study on the effect of amount of sliane coupling agent of the alumina filler and amount of alumina filler on mechanical properties of alumina reinforced methacrylate-based polymer.

3. The third part was to study on the effect of amount of sliane coupling agent on the alumina filler on color change of alumina reinforced methacrylate-based polymer.

CHAPTER III

RESEARCH METHODOLOGY

Part 1: The effect of various types of silane coupling agent and silanization process (solutions of different polarity) on alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

Materials used

      Two hundred and sixty two square-shaped plates (10×10×2 mm) were prepared from alumina square slabs (purity 99.7 mass%, SSA-S square plate, Nikkato Corp., Osaka, Japan) as the substrate. To decontaminate the surface, all alumina plates were soaked in the *piranha solution* (7:3 concentration H_2SO_4:H_2O_2) for 40 minutes to make a clean and fresh oxide layer [16], followed by rinsing with deionized water and dried for 24 hours at room temperature prior to silanization with one of the following three silane coupling agents; MPS, APS and AAPS. These commercial silane coupling agents were used as received. Three solutions were selected; 70 vol% ethanol solution mixture of 99.8 vol% ethanol and deionized water (ETH), 99.7 vol% isopropanol (ISP) and 99.5 vol% toluene (TOL). The silane coupling agents and solutions used are listed in Table 3.

Table 3 Silane coupling agents and solutions used in the present study

Name	Code	Brand or Cat. No.	Mfg.	Lot. No	Solubility parameter of organic functional group
Silane coupling agent					
3-methacryloxypropyl trimethoxysilane	MPS	KBM 503	Shin-Etsu Chemical Tokyo, Japan	03999	9.48
N-2 (aminoethyl) 3-aminopropyl triethoxysilane	AAPS	KBE 603	Shin-Etsu Chemical, Tokyo, Japan	503038	10.24
3- aminopropyl triethoxysilane	APS	KBE 903	Shin-Etsu Chemical, Tokyo, Japan	507147	9.86
Solution					
Ethanol	ETH*	414608	Carlo erba, Milan, Italy	V9M8OO259M	--
Isopropanol	ISP	41515	Carlo erba, Milan, Italy	V9C716129C	--
Toluene	TOL	488555	Carlo erba, Milan, Italy	6G717036I	--

*: ETH was diluted with 30% deionized water

Silanization Process

ETH, ISP, and TOL were used without further preparation except in mixing with MPS. ETH and ISP mixing with MPS were adjusted to a pH of 4.5 by titrating with 99.9% acetic acid (Carlo erba, Milan, Italy) using a pH meter (ORION 420A, Orion Research Inc., Boston, MA, USA). APS and AAPS were not adjusted because amino silane could initiate hydrolysis using moisture in the atmosphere. Three silane coupling agents were mixed with all solutions to achieve 2 vol% according to the previous studies [15, 75].

These solutions were stored in a 100 ml polyethylene cup with a cover and allowed to hydrolyze for 5 minutes. The alumina plate was soaked in the silane solution for 3 minutes. Then, the alumina plate was removed from the cup and left dry at room temperature for 14 days before undergoing the shear bond test. Alumina plates without immersion were served as a reference group.

Surface roughness analysis

The average roughness (Ra) of each silanized alumina plate was measured using a profilometer (TalyScan 150, Taylor Hobson Ltd., Leicester, UK). A contact stylus gauge was used to analyze roughness tracing. The measurement was achieved by scanning on the surface at a speed of 3,000 μm/s with a reading interval of 5 μm. The Ra was calculated from an alumina surface using software (TalyScan 150 software analyzer, Taylor Hobson Ltd). Two specimens of each condition were selected and six areas of each specimen were examined. Alumina plates without immersion and alumina plates after treated by the *piranha* solution were served as reference groups.

Contact angle analysis

The static contact angle of alumina plates with and without silanization was measured using a contact angle tester (DSA 10-MK2, Kruss Optronic, Hamburg, Germany). Silanized alumina plates were washed with tetrahydrofuran solution (THF, Carlo erba, Milan, Italy) 10 times to remove unreacted silane coupling agents. A 10-μL sessile droplet of de-ionized water was placed onto the alumina plate. The shape of the droplet after 3 minutes from the placement was measured to determine the contact angle. Two specimens of each condition were selected and three areas were examined. Alumina plates after treated by the *piranha* solution were served as a reference group.

Shear bond test

A double-sided adhesive tape (King Tape, Thai Adhesive Tapes Industry, Bangkok, Thailand; 35 μm in thickness) with a 6-mm diameter hole was fixed at the center of the alumina plate to define the bonding area. A polytetrafluoroethylene tube, 7 mm in diameter and 5 mm in height, was placed o

n the adhesive tape. Then auto-polymerized PMMA (Unifast Trad, GC Corp., Tokyo, Japan) was placed into the tube using the brush-on technique. All specimens were divided into two groups [non-thermocycling (non-TC), and thermocycling (TC)] with n=8 (Table 4). In the thermocycling group, specimens were alternatively immersed in 5^OC and 55^OC water with the 1-minute dwelling time for 10,000 cycles using a thermocycling apparatus (HWB332R, KMIT, Bangkok, Thailand). All specimens were stored in 37^OC distilled water for an additional of 24 hours prior to the shear bond test. The specimens were fixed in a special jig to align a chisel-shaped rod parallel to the bond surface at the bonding interface (Fig.7). The shear bond test was performed using a universal testing machine (model 8872, Instron, Fareham, UK) at a crosshead speed of 0.5mm/min until the PMMA cylinder came off. The failure force in Newton was recorded and divided the force with the bond surface area (mm^2) resulting in mega-pascals (MPa).

Figure 7 Shear bond test apparatus.

Table 4 Groups of specimens [Non-thermocycling (non-TC) and thermocycling (TC)].

Types and amount of silane	ETH (non-TC)	ETH (TC)	ISP (non-TC)	ISP (TC)	TOL (non-TC)	TOL (TC)
2% MPS	8	8	8	8	8	8
2% APS	8	8	8	8	8	8
2% AAPS	8	8	8	8	8	8
Reference (without immersion) in non-TC = 8						
Reference (without immersion) in TC = 8						

Fourier Transform Infrared Spectroscopy analysis (FTIR)

To confirm the existing of silane coupling agent layers deposited on alumina surfaces, silanized alumina surfaces were analyzed using a FTIR with an attenuated total reflectance device (Spectrum 100, PerkinElmer Inc., Madison, WI, USA), taking 32 scans at wave numbers from 400 to 4,000 cm^{-1}. Prior to the FTIR analysis, 3 silanized alumina plates for each condition were immersed and washed with THF. This procedure was repeated until THF supernatant showed only absorbance peak at 250 nm on spectrophotometer (Nicolet Evolution 500, Thermoelectron Corp., Madison, WI, USA). The alumina surfaces after the shear bond test were also analyzed without THF washing. Three measurements of each specimen were performed.

Element deposition analysis

To elucidate the effectiveness of silane deposited on the alumina surface, alumina plates after silanization were undergone with tetrahydrofuran (THF, Carlo erba, Milan, Italy) washing. This procedure was repeated until THF supernatant showed only

absorbance peak at 250 nm on spectrophotometer (Nicolet Evolution 500, Thermoelectron Corp., Madison, WI, USA). Silanized alumina plates after THF washing and fractured surface after the shear bond test with non-thermocycling and after thermocycling were analyzed by a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) (JSM-5410LV, JEOL, Tokyo, Japan). A thin layer of carbon was evaporated onto the bonded area to avoid surface charging before observation. The primary electron beam energy was operated at 20 keV for each specimen. Three areas of 2.5 x 1.9 mm, at the center of the specimen, were examined. The surfaces of the untreated condition were also analyzed as a reference group. Three specimens for each condition were performed.

Statistical analysis

A 3-way analysis of variance (3-way ANOVA) was applied for evaluating the interaction among silane coupling agent, solution and thermocycling challenge on the shear bond strengths. Tukey HSD's test was used for comparing all conditions of shear bond strengths. The surface roughness and contact angle analysis were statistically analyzed with one-way ANOVA. All of the data were analyzed by statistical software (SPSS ver. 16, SPSS Inc., Chicago, Ill., USA). Statistical significant was set at α =0.05.

Part 2: Effect of amount of sliane coupling agent on the alumina filler and amount of silanized alumina filler on mechanical properties of methacrylate-based polymer.

Silanization of alumina particle

The silane coupling agent and solution used in Part 2 were selected from the results of the study from Part 1. Spherical-shaped alumina particle with a diameter ranged from 18-23μm (AH35-2, MICRON, Himeji-shi, Hyogo-ken, Japan; surface area of 0.36 m^2/g) was selected as a filler. The filler was silanized with MPS (KBM 503, Shin-Etsu Chemical, Tokyo, Japan). The amounts of MPS used in this study were 0.1, 0.2 and 0.4 mass%. The 0.1 mass% of MPS was expected to create monolayer of silane coating on the filler surface based on Arkle's equation [17] as follows:

$$\text{Amount of silane (g)} \quad = \quad \frac{\text{Amount of filler (g) x Surface area (m}^2\text{/g)}}{\text{Minimum coating area of silane coupling agent (m}^2\text{/g)}}$$

where, the minimum coverage area of MPS is 314 m^2/g.

One hundred milliliters of ethanol aqueous solution (70 vol%) was prepared using 99.8 vol% ethanol (Carlo erba, Rodano, Milano, Italy) and deionized water, and adjusted to a pH of 4.5 by titrating with 99.9% acetic acid (Carlo erba, Milan, Italy) using a pH meter (ORION 420A, Orion Research Inc., Boston, MA, USA). Then, 0.1, 0.2, or 0.4 g of MPS were added into the ethanol aqueous solution, and stirred. This MPS solution was stored in a 100 ml polyethylene cup with a cover, and allowed 5 minutes for hydrolysis and silanol formation. Then, 100g of alumina fillers were added into each MPS solution. The mixture was stirred until the solution was completely evaporated, and left dried at room temperature for 14 days [8]. Alumina particle without this silanization was used as the 0.0 mass% MPS group.

Element deposition analysis

To elucidate the effectiveness of silane deposited on the alumina filler, a scanning electron microscope (SEM, JSM-5410LV, JEOL, Tokyo, Japan) with energy dispersive spectrometer (EDS; EDS software) was used to detect silicon (Si) on the surface of alumina filler. Prior to energy dispersive spectrometer analysis, some amounts of all silanized and non-silanized groups were washed with tetrahydrofuran (THF, Carlo erba, Rodano, Milano, Italy). This procedure was repeated until THF supernatant showed only absorbance peak at 250 nm on spectrophotometer (Nicolet Evolution 500, Thermoelectron Corp., WI, USA). Both alumina particles before and after THF washing were analyzed by EDS. A thin layer of carbon was evaporated onto the surface before analyzing. The primary electron beam energy was operated at 20 keV. The electron beam spot on the specimen with a collection time of 100 seconds were used.

Thermal Analysis / Thermo gravimetric Analysis (TGA)

TGA was used to measure the amount and rate of weight changing from burning process of silane coupling agent which silanized onto the alumina filler. The amount of 7 mg of silanized alumina filler before and after THF washing in all groups were analyzed by thermo gravimetric analyzer (TGA-Q50, TA instrument, New Castle, DE, USA) with a heat rate of 10°C per min, and an air flow rate of 10 mL per 90 min. The temperature of the analyzer was started at room temperatures until thermal stability was up to 800°C.

Specimen preparation for 3-point bending and wear tests

A heat-polymerized PMMA (Triplex hot, Ivoclar Vivadent AG, Schaan, Liechtenstein) was used as the PMMA base. The alumina filler prepared as above-mentioned manner was mixed with the PMMA base to be 10, 30, 50 mass% using a sun-and-planet movement mixer (Non bubbling kneader, NBK-1, Nippon Seiki, Tokyo, Japan) (table 5). Bar-shaped (65 x 10 x 2.5 mm) (ISO 1567: Specifications for denture

base polymers) and square-shaped (10 x 10 x 2.5 mm) wax patterns were prepared for the 3-point bending and the wear tests, respectively. Specimens for tests were prepared following a conventional compressive process. PMMA-based powder and monomer was mixed at a powder/liquid ratio of 2.3/1 by weight. After the dough stage, the mixture was placed in the flask, pressed and heat-polymerized with a long curing cycle (74°C for 8 h). Subsequently, after the flask was cooled to room temperature, all specimens were deflasked and polished with silicon carbide abrasive paper from # 600, 800, 1,000 to 1,200 with water. The specimens were immersed in 37^{0}C distilled water for 24 hours prior to the test. Specimens of PMMA without fillers were also prepared as a reference group (No filler group). The groups of specimen for flexural properties and wear resistance test were shown in Table 5.

Table 5 Specimen groups for flexural properties and wear resistance test.

Amount of silane (mass% of MPS)	% of Alumina filler		
	10%	30%	50%
0 mass%	10	10	10
0.1 mass%	10	10	10
0.2 mass%	10	10	10
0.4 mass%	10	10	10
Control group (unreinforced) = 10			

Three-point bending test

Flexural properties (flexural strength and modulus) were determined by the 3-point bending test using a universal testing machine (Instron 8872, Fareham, UK) with a crosshead speed of 5 mm/min and a support span width of 50 mm until specimen fracture. The dimensions of the specimen were measured using a digital micrometer (minimum reading: 0.001mm, Digimatic Micrometer, Mitutoyo Corp., Kanagawa, Japan)

before the test. Flexural strength (σ_f) and flexural modulus (E_f) were calculated according to the formula:

$$\text{Flexural strength } (\sigma_f) = 3FL / 2BH^2$$

$$\text{Flexural modulus } (E_f) = L^3m/4BH^3$$

where,   F = the maximum load (N) in the load - displacement curve.

            L = the support span width (50.0 mm)

            B = the width of the specimen (mm)

            H = the thickness of the specimen (mm)

            m = the gradient (slope) of the initial straight-line portion of the load

                deflection curve (N/mm)

Ten specimens of each condition were examined.

Wear test

The *in-vitro* 2-body wear-testing apparatus based upon a rotary pin-on-disc design [76] (Fig. 8) was used to determine the wear resistance. The fine finishing stone bur (micro grained aluminum oxide grit: Dura-White[®] Stones, Shofu, Kyoto, Japan) (diameter 3 mm) (Ra 2.28 µm) was used as the antagonist. The antagonist was vertically loaded with 15 N and undergone 10,000 cycles at 1,000 rpm on the specimen surface without lateral movement. No chemical or abrasive medium was used during the wear testing. All wear tests were performed at room temperature with continuously flow of distilled water through the specimen. After the wear test, the specimen was removed from the apparatus, and the surface was cleaned with distilled water. The volume loss of each specimen was measured using a profilometer (TalyScan 150, Taylor Hobson Ltd., Leicester, UK). A contact stylus gauge was used to analyze wear trace. The instrument scans at a speed of 3,000 µm/s with a reading interval of 5 µm. The amount of volume loss was calculated from a depth of wear surface using software (TalyScan 150 software analyzer, Taylor Hobson Ltd). Ten specimens of each condition were examined.

Figure 8 2-body wear-testing apparatus

Microstructure observation of the surfaces after test

Microstructure of the fracture and wear surfaces of 3 specimens of each condition after gold sputtering were observed using the SEM at an acceleration voltage of 15 kV.

Statistical analysis

Flexural strength, flexural modulus and volume loss were analyzed by two-way analysis of variance (2-way ANOVA), Dunnett T3 and Tamhane's test was used for comparing all groups by statistical software (SPSS ver, 16, SPSS Inc., Chicago, Ill., USA). Statistical significant was set at α=0.05.

Fracture toughness test

Specimen preparation for fracture toughness test

The silane coupling agent and technique of silanization used were selected from the result of Part 1. The amounts of alumina fillers were prepared as follows; 0%, 10%, 30% and 50% weight. The amount of silane coupling agent was selected from the result of the flexural strength test (0.1 mass% of MPS). Heat-polymerizing PMMA was

used as the PMMA base (the same as for the flexural strength test). The alumina filler prepared as above-mentioned manner was mixed with the PMMA base to be 10, 30, 50 mass% using a sun-and-planet movement mixer (Non bubbling kneader, NBK-1, Nippon Seiki, Tokyo, Japan). Bar-shaped specimens were prepared according to ISO 20795-1: 2008 (for denture base polymer). Wax patterns were prepared for the 3-point bending test with a single edge-notched. Specimens for tests were prepared following a conventional compressive process. PMMA-based powder and monomer was mixed at a powder/liquid ratio of 2.3/1 by weight. After the dough stage, the mixture was placed in the flask, pressed and heat-polymerized with a long curing cycle ($74^{o}C$ for 8 h). Subsequently, after the flask was cooled to room temperature, the specimens were deflasked and polished with silicon carbide abrasive paper from # 600, 800, 1,000 to 1,200 with water. Single edge-notched compact specimens were prepared by notched machine with 3.0 mm in depth. The specimen dimensions and shape (ISO 20795-1:2008) are shown in Figure 8. The specimens were immersed in $37^{o}C$ distilled water for 24 hours prior to the test. Specimens of PMMA without the filler were also prepared as a reference group (No filler group). A total number of forty specimens (n=10) were prepared (Table 6).

Table 6 Specimens groups for fracture toughness test.

% of alumina filler	Amount of silane (from flexural strength test)
	(N)
10%	10
30%	10
50%	10
Control group (unreinforced) = 10	

To determine the fracture toughness (K_{ic}), specimens were placed on a universal testing machine (Instron 8872, Fareham, UK) for the 3-point bending jig at a crosshead speed of 1 mm/min until fracture. Peak load to fracture was recorded. The accumulated data were used to determine the fracture toughness (K_{ic}) in MPa·m$^{1/2}$.

Flexural toughness (K_{ic}) was calculated according to the formula:

$$K_{max} = f\, P_{max} l_t\, /\, (b_t h_t^{3/2}) \times \sqrt{10^{-3}} \qquad \text{MPa·m}^{1/2}$$

where,

f is a geometrical function dependent on x

$f(x) = 3x^{1/2}[1.99-x(1-x)(2.15-3.95x+2.7x^2)/[2(1+2x)(1-x)^{3/2}]$

and

$x = a/h_t$

P_{max} is the maximum load exerted on the specimen, in newtons;

Height $h_t = 8.0 \pm 0.2$ mm

Width $b_t = 4.0 \pm 0.2$ mm

Pre-crack $a = 3.0 \pm 0.2$ mm

Span $l_t = 32.0 \pm 0.1$ mm
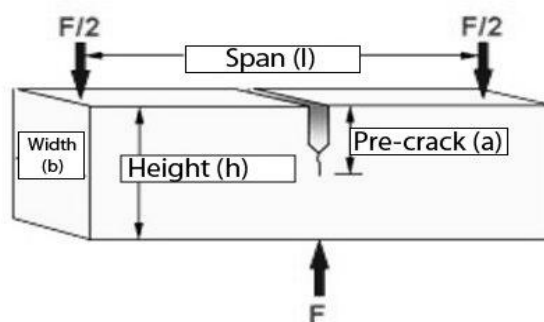
Figure 9 General single edge notch bend specimen dimensions for test specimens.

Statistical analysis

   Fracture toughness was analyzed by one-way analysis of variance (1-way ANOVA) and Tukey HSD test was used for comparing all groups by statistical software (SPSS ver, 16, SPSS Inc., Chicago, Ill., USA). Statistical significant was set at α=0.05.

Part 3: Effects of amount of sliane coupling agent on the alumina filler on color change of methacrylate-based polymer.

Preparation of the specimens

The pink heat-polymerized PMMA (Triplex hot, Ivoclar Vivadent AG, Schaan, Liechtenstein) and clear heat-polymerizied PMMA (ProBase Hot, Ivoclar Vivadent AG, Schaan, Liechtenstein) were commercial products. All of these groups were prepared by using alumina fillers with silanization process as the same method as part 2.

PMMA-based specimens, containing 10 mass% without silanized alumina filler and with silanized alumina fillers of 0.1, 0.2 and 0.4 mass% of MPS for the color change test were blended with heat-polymerized PMMA. For the pink heat-polymerized PMMA, the powder was sieved to separate the color of the fiber, to eliminate the factor which affected the color of PMMA powder. PMMA specimen without alumina reinforced was served as the reference group. The powder/liquid (P/L) ratio of the denture base resins both in the unreinforced and alumina filler-reinforced groups were 2.3/1 by weight. After the dough stage, the resin was pressed into the flask and heat-polymerized with a long curing cycle ($74^{\circ}C$ for 8 h). Subsequently, after the flask was cooled to room temperature, the specimens were deflasked and wet polished with silicon carbide abrasive paper from # 600, 800, 1,000 to 1,200. The specimens were prepared in squared-shaped, 15X15 mm and 2 mm in thickness. A totally number of one hundred specimens (n=10) were prepared (table 7). The specimens were immersed in $37^{0}C$ distilled water for 24 h prior to the color change test.

Color change test by spectrophotometer

The CIE L*a*b color system was used to measure the color of the samples in reflected light on black and white background with a spectrophotometer (Ultrascan XE, Hunter Lab, Reston, VA, USA). The spectrophotometer, using standard illuminant D65 with 10° viewing angle, was calibrated using black and white standards. Specimen orientation

against the spectrophotometer head was standardized by a specimen holder. The measurements were performed according to the CIE L*a*b* system and the mean L*, a* and b* values for each material were repeated. The total color change obtained was calculated for each specimen. The groups of specimens for the color change test were shown in Table 7.

Table 7 Groups of specimens for the color change test.

amount of silane	10% of alumina filler reinforced into pink PMMA	10% of alumina filler reinforced into clear PMMA
0%	10	10
0.1%	10	10
0.2%	10	10
0.4%	10	10
Control group (unreinforced)	10	10

Statistical analysis

The total color change obtained was calculated for each specimen using the equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where ΔL^*, Δa^* and Δb^* are different values between the unreinforced group (reference) and reinforced alumina fillers, which silanized with different amounts of MPS. Color changes were considered visually perceptible when $\Delta E > 1$ and clinically acceptable when $\Delta E < 3.3$. Additionally, the opacities values were analyzed by one-way analysis of variance (1-way ANOVA), Tukey HSD and Tamhane's test was used for comparing all groups by statistical software (SPSS ver, 16, SPSS Inc., Chicago, Ill., USA). Statistical significant was set at $\alpha = 0.05$.

CHAPTER IV

RESULTS

Part 1: The effect of various types of silane coupling agent and silanization process (solutions of different polarity) of alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

Surface roughness analysis

Results of the average surface roughness (Ra) of various silanized conditions are summarized in Table 8. From the statistical analysis, the surface roughness of all conditions was not significantly different except for MPS in ETH and AAPS in TOL, which were smaller than that of after *piranha solution*. This result indicated that the surface after silanization was smoother than that of before silanization.

Table 8 Average surface roughness (standard deviations) in micron (μm) of various silanized conditions (n=12).

Silane coupling agents	Solution		
	Ethanol Sol[n]	Isopropanol	Toluene
MPS	0.139 (0.006) [b]	0.136 (0.006) [a,b]	0.132 (0.014) [a,b]
AAPS	0.139 (0.143) [a,b]	0.133 (0.005) [a,b]	0.129 (0.005) [a]
APS	0.131 (0.012) [a,b]	0.134 (0.007) [a,b]	0.131 (0.006) [a,b]
Control Ra alumina	0.144 (0.019) [a,b]		
After *piranha solution*	0.186 (0.009) [c]		

Values with the same letters are not statistically significant different ($p<0.05$)

Contact angle analysis

Results of contact angles of various silanized conditions are summarized in Table 9 and Figure 10. The contact angle of the untreated condition was 85.8º. The contact angles of alumina plates immersed in solutions without silane coupling agents were almost identical to that of the untreated condition. The contact angles after silanization with various conditions were quite different. Two-way ANOVA revealed that two main factors which were type of silane coupling agent and solution and their interactions were significant. Tamhane's test indicated that the contact angles of silanized with MPS, AAPS and APS were significantly smaller than that of untreated condition, and the contact angle of silanized with MPS in ethanol solution was the smallest.

Table 9 Contact angles (standard deviations) in degree (º) of various silanized conditions (n=6).

Silane coupling agents	Solution			
	Ethanol Sol^n	Isopropanol	Toluene	Without
MPS	56.4 (3.3)^a	65.9 (4.5)^b	64.3 (4.3)^b	--
AAPS	73.7 (2.7)^c	74.2 (2.4)^c	75.9 (3.2)^c	--
APS	67.0 (4.4)^b	75.3 (2.1)^c	77.9 (2.3)^c	--
Without	--	--	--	85.8 (0.9)^d

Values with the same letters are not statistically significant different ($p < 0.05$)
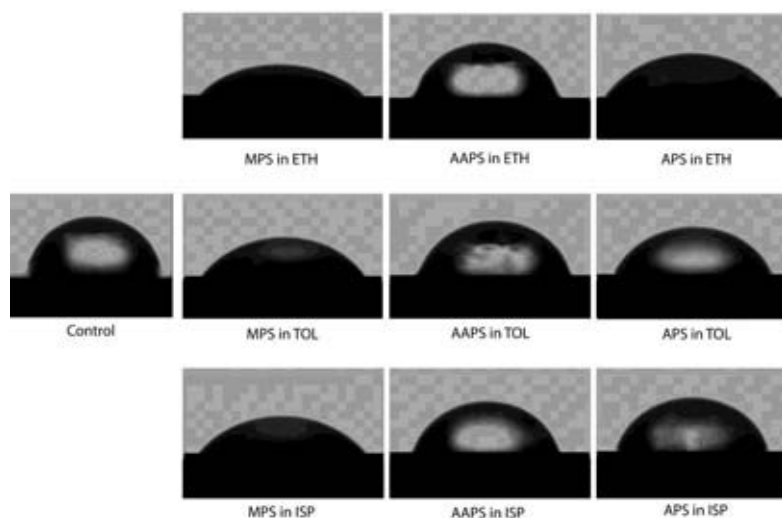
Figure 10 Contact angles of all conditions.

Shear bond strength

There was no obvious PMMA remaining on alumina surfaces after the shear bond test. The shear bond strengths of various silanized conditions are summarized in Figure 11. Relationship between shear bond strengths and solubility parameters are summarized in Figure 12. Three-way ANOVA revealed that the three main factors (silane coupling agents, solutions and thermocycling challenge) and their interactions were significant. Therefore, Tukey HSD's test was performed to compare all conditions including untreated conditions. Regarding non-themocyclings, the shear bond strengths after silanization were significantly greater than that of the untreated condition; the shear bond strengths of MPS in ETH (15.0 MPa) and APS in ETH (13.8 MPa) were significantly greater than the other conditions. After thermocyclings, the shear bond strengths of each condition were significantly smaller than those of the corresponding condition non-thermocycling except for the untreated conditions. The bond strengths in ETH were significantly greater than those in ISP and TOL ($p < 0.05$). The solubility parameter of MMA and PMMA are 9.2 and 8.75, respectively [75-78]. The smaller solubility parameter which was MPS in this study showed the greater shear bond strength.
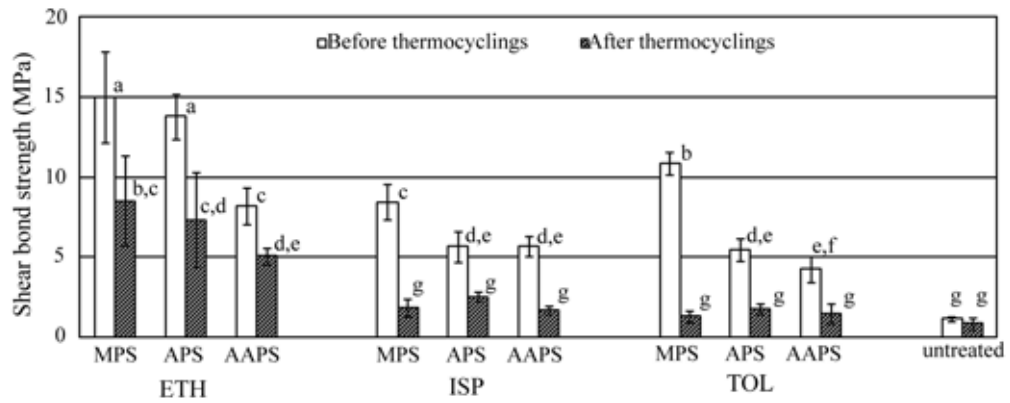
Figure 11 Shear bond strengths of PMMA and alumina plates.

Error bars indicate standard deviations; values with the same letters

are not statistically significant different ($p < 0.05$).

Figure 12 Relationship between shear bond strengths and solubility parameters.

A: Non-thermocyclings, B: after thermocyclings

Error bars indicate standard deviations; values with the same letters

are not statistically significant different ($p < 0.05$).

FTIR on alumina plate

Typical FTIR spectra of silanized alumina plates after shear bond test are demonstrated in Figure 13. There were no obvious differences in the FTIR spectrum between specimen undergone THF washing and the shear bond test when using the same silane coupling agent and solution. In the MPS-treated group, transmittance peaks of symmetric C–H stretch of the CH_3 group (2,937 cm^{-1}), symmetric C–H stretch of the C=O group (2,841 cm^{-1}), symmetric C=O stretch (1,719 and 1,638 cm^{-1}), and asymmetric Si–O–Si stretching (1,086–1,083 cm^{-1}) were observed. On the other hand, in the AAPS and the APS treated group, transmittance peaks of N–H bend (1,495–1,448 cm^{-1}) and only asymmetric Si–O–Si stretching (1,089–1,077 cm^{-1}) were observed. These results suggested that silane coupling agents were remained on alumina plate surface after THF washing and the shear bond test, indicating the effectiveness of silane coupling agents used in silanization of the alumina.
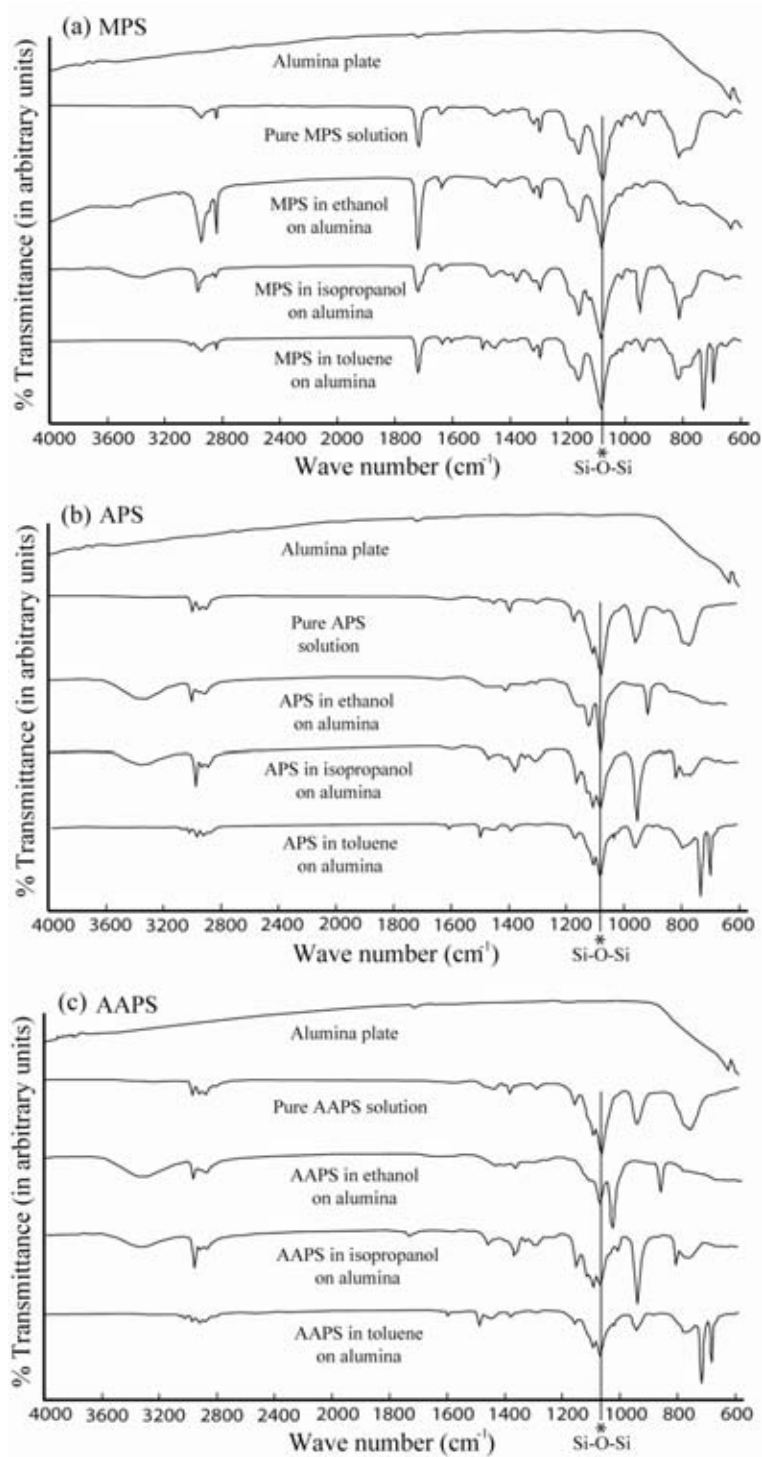
Figure 13 Typical FTIR spectra of silanized alumina plates after

the shear bond test: (a) treated by MPS, (b) treated by APS,

(c) treated by AAPS.

Element deposition analysis

The EDS analysis revealed that carbon, oxygen, aluminium (Al), and silicon (Si) were detected on the silanized alumina surfaces after THF washing and the alumina surface where PMMA was removed after the shear bond test of all silanized groups. Mass compositions of Al and Si are summarized in Table 10. Si element could not be detected from the alumina surface of the untreated condition, but 2.1-5.2 mass% of Si was detected on the silanized alumina after THF washing. The same amount was detected on specimens after the shear bond test with non-thermocyclings (1.9-4.8 mass%). However, the amount of Si element decreased on the silanized alumina groups after the shear bond test (1.6-2.5 mass%). From this table, the existence of silicon after THF washing suggested that silane coupling agent could not be removed by THF washing. In addition, the silicon was detected from fracture surfaces of specimens after thermocyclings indicated that silane coupling agent remained on the alumina plate after the shear bond test.

The elements mapping of MPS specimens in all solutions on fracture surfaces after the shear bond test specimens undergone thermocyclings are demonstrated in Figure 14, which was similar to those of APS and AAPS specimens. Determining the EDS mapping, in untreated condition surface image shows only aluminium but not the silicon show, in contrast with in the other images which can be seen both of aluminium and silicon.

These results suggested that silane coupling agent reacted with the alumina plate and remained after the shear bond test.

Table 10 Elemental compositions on silanized alumina plates after THF washing and the shear bond test.

Silanized condition	Percentage of elements composition at atomic %					
	THF washing (before shear bond test)		After shear bond test			
	Al	Si	Al		Si	
			Non-thermocycling	Thermocycling	Non-thermocycling	Thermocycling
Untreated	100.0	0.0	100.0	100.0	0.0	0.0
MPS in ETH	95.8 (0.8)	4.2 (0.8)	95.9 (0.8)	97.5 (0.5)	4.1 (0.8)	2.5 (0.5)
MPS in ISP	97.1 (0.4)	2.9 (0.4)	97.9 (0.4)	98.1 (0.2)	2.1 (0.4)	1.9 (0.2)
MPS in TOL	96.1 (0.9)	3.9 (0.9)	96.2 (0.9)	97.6 (0.1)	3.8 (0.9)	2.4 (0.2)
APS in ETH	95.5 (0.9)	4.5 (0.9)	95.8 (0.3)	98.0 (0.8)	4.2 (0.4)	2.0 (0.8)
APS in ISP	97.2 (0.4)	2.8 (0.4)	97.0 (1.1)	98.2 (0.3)	3.0 (1.1)	1.8 (0.3)
APS in TOL	97.0 (0.3)	3.0 (0.3)	97.1 (0.3)	98.2 (0.3)	2.9 (0.3)	1.8 (0.4)
AAPS in ETH	94.8 (0.3)	5.2 (0.4)	95.2 (0.6)	97.9 (0.3)	4.8 (0.7)	2.1 (0.3)
AAPS in ISO	97.9 (0.2)	2.1 (0.2)	98.1 (0.3)	98.3 (0.5)	1.9 (0.3)	1.7 (0.5)
AAPS in TOL	96.9 (0.2)	3.1 (0.2)	98.0 (0.2)	98.4 (0.3)	2.0 (0.2)	1.6 (0.3)
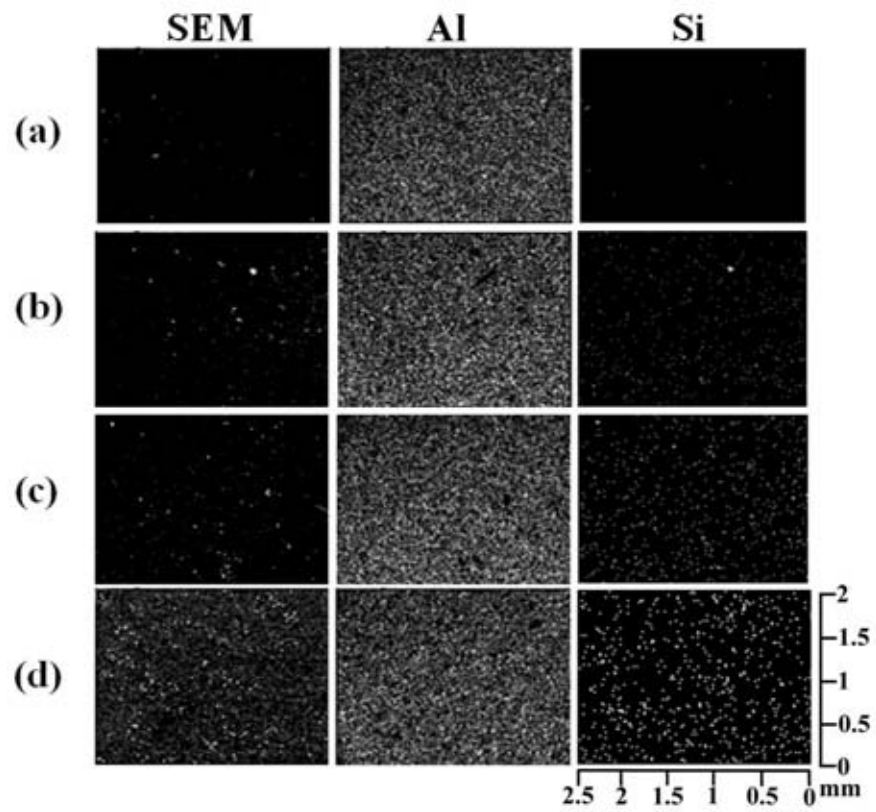
Figure 14 SEM images and Si and Al distribution on the fracture surface of MPS
     after the shear bond test.
     (a): untreated condition, (b): MPS in ethanol, (c): MPS in isopropanol,
     (d): MPS in toluene.

Part 2: The effect of silane coupling agent on alumina filler and mechanical properties of methacrylate base using alumina filler.

From the silicon deposition analysis (Table 11), Si was detected in all silanized groups, while Si could not be detected in the non-silanized group. The amount of detected Si increased with an increase of MPS, but did not proportionally increase. The amount of detected Si decreased after THF washing, and these values were almost constant regardless of MPS amount.

Table 11 Mean percentage of elements composition in silanized alumina fillers (n=3).

	Mass Percentage of elements composition (SD)			
	Al		Si	
Specimen	Non-THF washing	After THF washing	Non-THF washing	After THF washing
0.0% MPS	100.0 (0.0)	100.0 (0.0)	--	--
0.1% MPS	96.2 (0.6)	96.4 (0.5)	3.8 (0.6)	3.6 (0.5)
0.2% MPS	93.2 (0.4)	96.0 (0.7)	6.8 (0.4)	4.0 (0.7)
0.4% MPS	88.2 (0.6)	95.8 (1.0)	11.8 (0.6)	4.2 (1.0)

From the thermogravimetric analysis, the percentages of weight loss after the heat treatment are demonstrated in Table 12. In non-THF washing, the weight loss of 0.4 mass% MPS group was higher than that of the other groups. In contrast with after THF washing, the percentage of weight loss of the 0.4 mass% MPS group was similar to the 0.1 and 0.2 mass% MPS groups.

Table 12 Percentages of weight loss in alumina fillers after TGA analysis.

Specimen	Weight loss (%)	
	Non-THF washing	After THF washing
0.0% MPS	0.11	--
0.1% MPS	0.63	0.56
0.2% MPS	1.13	0.43
0.4% MPS	1.78	0.48

The flexural strength, flexural modulus and volume loss are summarized in Figure 15-19.

For flexural strength test, on the main factors of amount of silane coupling agent and amount of alumina powder were significant, but their interactions were not.

Flexural strengths ranged from 95.1 to 115.8 MPa (Figure 15). From the statistical analysis, determining the effect of amount of silane in all of alumina filler groups, the flexural strengths of all silanized groups were greater than those of the No filler and the 0.0 mass% MPS group. For the flexural strengths of 10% alumina were significant difference from those of control, 30% and 50% alumina groups.

The flexural moduli ranged from 3.09 to 3.89 GPa. From the two-way ANOVA statistical analysis, the interaction between amount of silane coupling agent and amount of alumina powder was significant. The flexural moduli of 0.1 mass % MPS conditions were significantly greater than that of the control. In addition, regarding 50% groups, flexural moduli were significant greater than control group.

From wear test, volume losses ranged from 0.038 to 0.160 mm^3. Generally, the higher volume loss means the poor wear resistance. From this study, the volume loss of no filler group was the greatest. Comparing with the no filler group, the alumina reinforced group was smaller. From two-way ANOVA statistical analysis, it showed that the interaction between amount of silane coupling agent and amount of alumina powder was significant. Therefore, comparison of all data including unreinforced group was

performed. The volume loss decreased when alumina powder was mixed. Moreover, the wear of silanized alumina group showed smaller than that of control group. These results suggested that alumina powder improve the wear resistance, moreover, silanization of alumina was also effective to improve wear resistance.
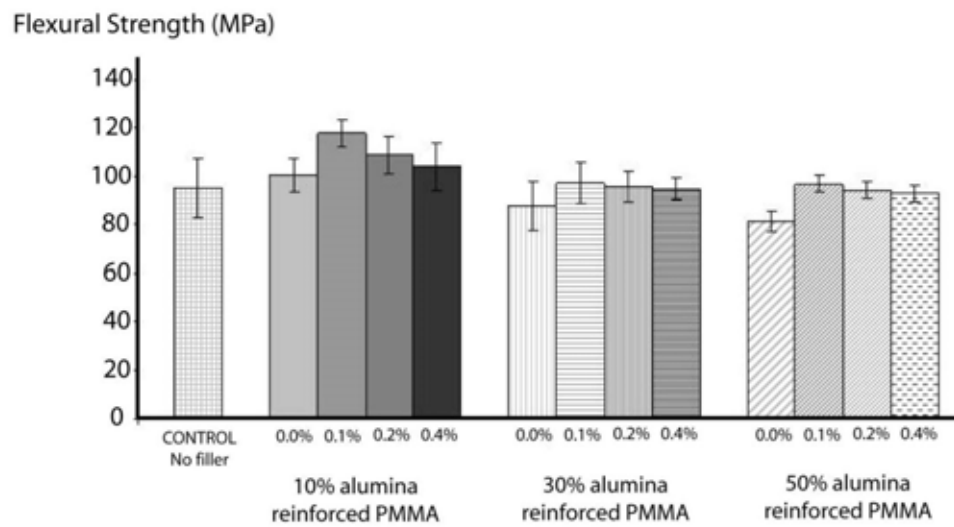
Figure 15 Flexural strengths of PMMA in all conditions.

Error bars indicate standard deviations.
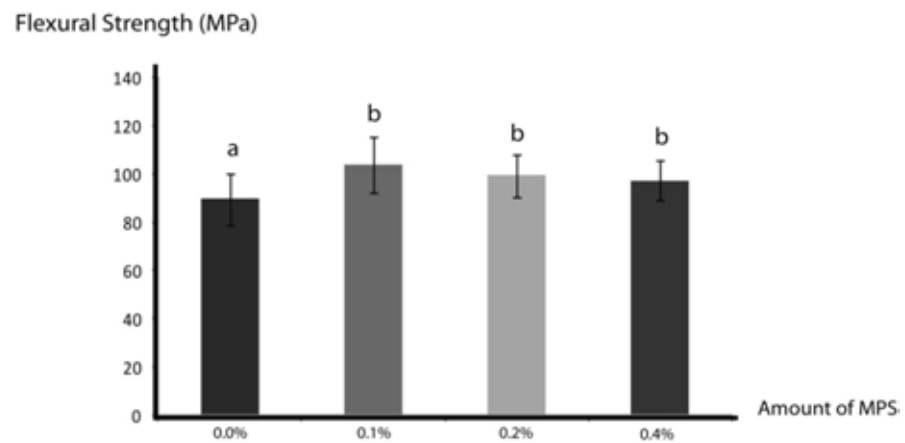
Figure 16 Flexural strengths of PMMA (determining the effect of amount of silane in all
of alumina filler reinforced PMMA groups).

Error bars indicate standard deviations; values with the same letters
are not statistically significant different ($p<0.05$).
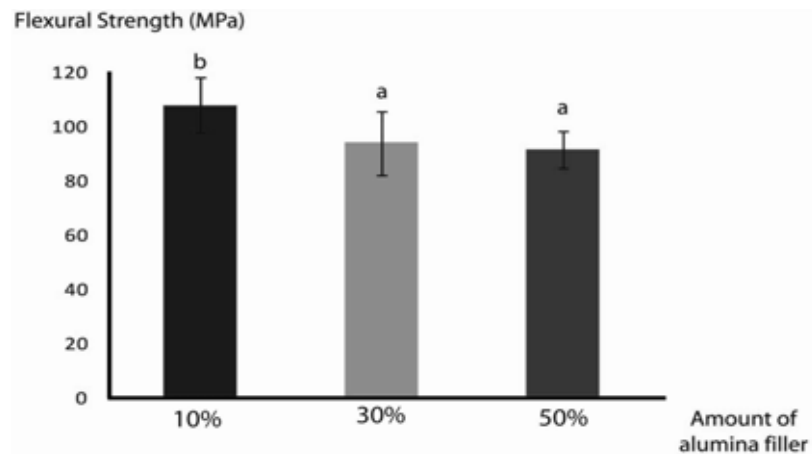
Figure 17 Flexural strengths of PMMA (determining the effect of amount alumina filler

reinforced PMMA in all of silane coupling agent groups).

Error bars indicate standard deviations; values with the same letters

are not statistically significant different ($p<0.05$).
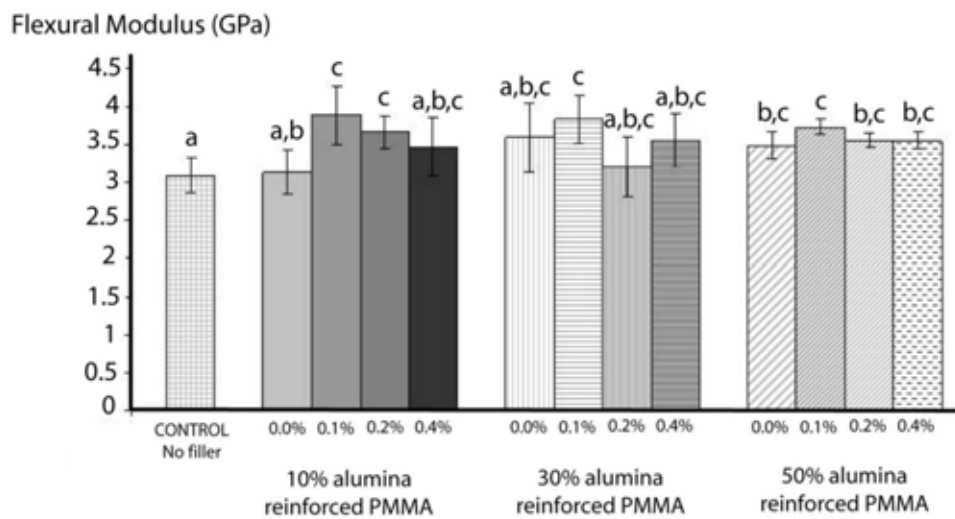
Figure 18 Flexural modulus of PMMA.

Error bars indicate standard deviations; values with the same letters

are not statistically significant different ($p<0.05$).
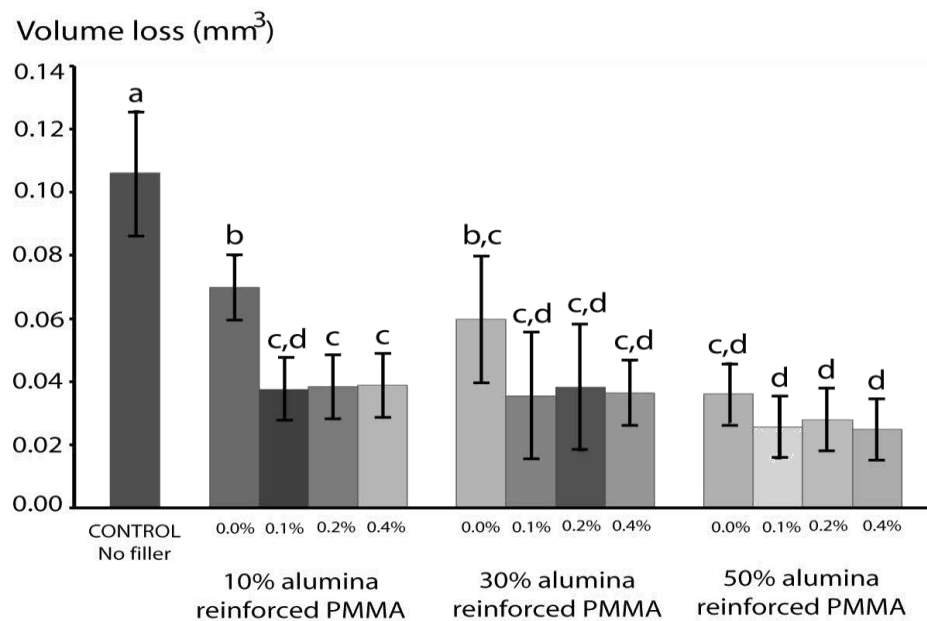
Figure 19 Volume loss of PMMA.

      Error bars indicate standard deviations; values with the same letters

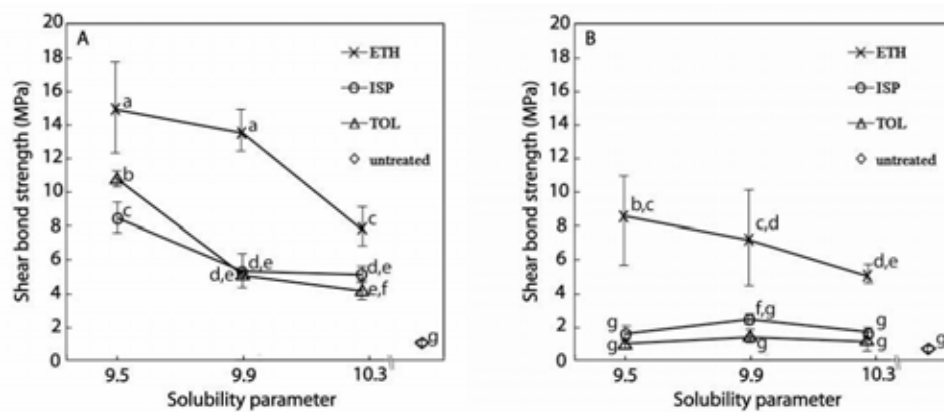   are not statistically significant different ($p<0.05$).

The SEM images of the 10 mass% group of PMMA surfaces after the 3-point bending test and wear test are shown in Figure 20. Fracture surfaces of the No filler group showed cohesive fracture of the PMMA beads. Exposures of alumina filler with the gap between the filler and PMMA were observed in the 0.0 mass% MPS group (Fig. 20B), but alumina fillers covered with resin were observed in the 0.1, 0.2, and 0.4 mass% MPS groups. Fracture surface in all silanized groups, gaps were not observed between alumina fillers and PMMA matrix.

The worn surfaces of the wear test showed circle with circular wear trace, which was created by antagonist rotation. In the No filler group, deep wear traces and some cracks were clearly observed. Shallow wear traces with exfoliated alumina particles (arrow head) and reducing of wear at the filler area (arrow point) were observed in the 0.0 mass% MPS group (Fig. 20G), while shallower wear traces without exfoliation of alumina particles and some cracks were observed in the 0.1, 0.2, 0.4 mass % MPS groups (Fig. 20H-20J). The SEM image of the 30 and 50 mass% groups were as the same as that of the 10 mass% group.
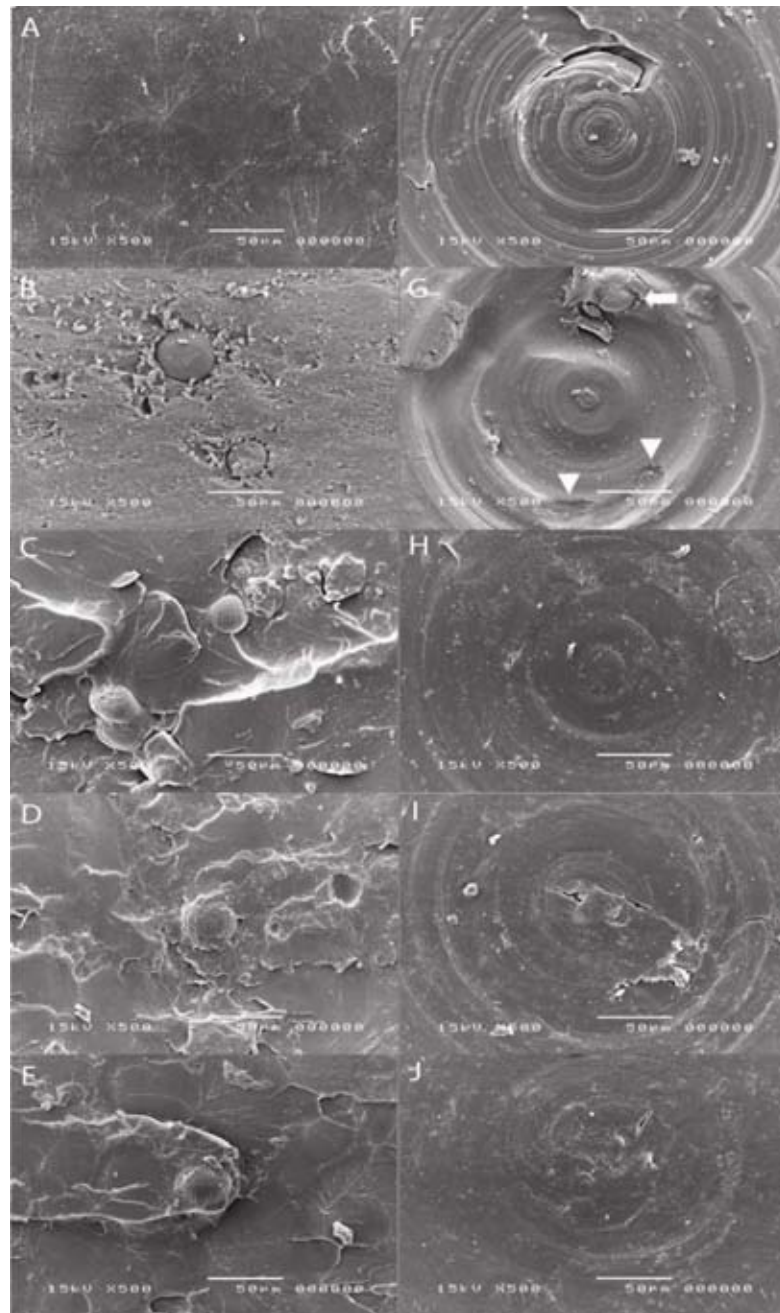
Figure 20 SEM images of the 10mass% group of PMMA surfaces after the 3-point

bending test and the wear test.

(A, F demonstrated pure PMMA; B, G were 0.0 mass%;

C, H were 0.1 mass%; D, I were 0.2 mass% and

E, J were 0.4 mass% of MPS silanized alumina filler reinforced PMMA).

The fracture toughnesses (K_{ic}) are demonstrated in Figure 21. Fracture toughness ranged from 1.94 to 2.64 MPa m$^{1/2}$. One-way ANOVA showed the significant difference among groups. In addition, the Tukey HSD comparison indicated the significant difference between 50% silanized alumina and control groups.
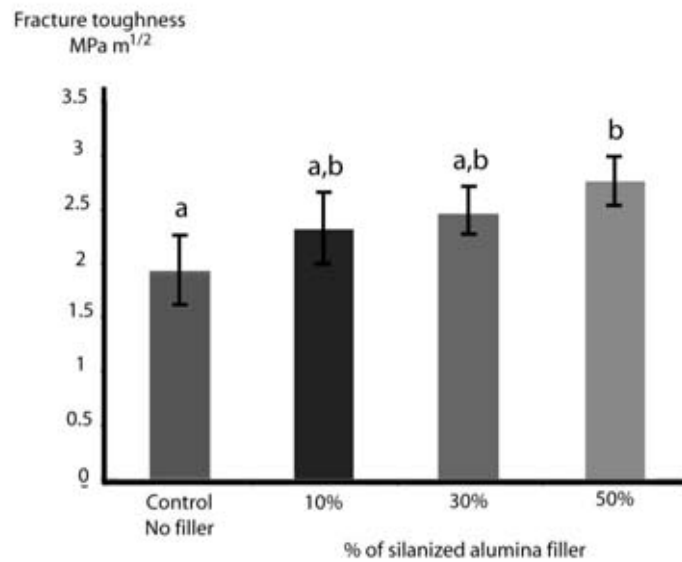
Figure 21 Fracture toughness of silanized with different mass% of alumina filler
          reinforced PMMA.
          Error bars indicate standard deviations; values with the same letters
          are not statistically significant different ($p<0.05$).

Part 3: The effects of amount of sliane coupling agent of the alumina filler on color change of methacrylate-based polymer.

The opacities value and color changes (ΔE) are summarized in Table 13. In pink and clear heat-polymerized PMMA groups, the opacities value of the No filler pink PMMA group (79.65%) and the No filler clear PMMA group (38.63%) were significantly lower than the other groups (p<0.05). In the pink PMMA groups, the opacity value of 0.0 mass% MPS group was significantly greater than the other groups. In clear PMMA groups, the opacity value of the 0.1 mass% MPS group was significantly greater than those of the control and the 0.2 mass% MPS groups (p<0.05). Additionally, the ΔE values of silanized pink PMMA were smaller than the 0.0 mass% MPS group. While in clear PMMA groups, the ΔE values of 0.1 mass% MPS group was quite similar with the 0.0 mass% MPS group. The specimens of opacity and color stability of pink and clear PMMA were demonstrated in Figure 22.

Table 13 Opacities and color changes (ΔE) of all test groups.

Condition	Opacities of pink PMMA	ΔE, ΔL, Δa, Δb of pink PMMA	Opacities of clear PMMA	ΔE, ΔL, Δa, Δb of clear PMMA
No filler	79.65 (1.14) [a]	--	38.63 (3.28) [e]	--
0.0 mass% MPS	93.16 (0.91) [d]	9.55, -7.96, 3.54, 3.92	79.07 (1.31) [g]	10.52, -10.46, 0.19, -0.79
0.1 mass% MPS	88.35 (1.42) [b]	5.89, -5.26, 1.93, 1.82	79.68 (1.37) [g]	10.48, -10.44, 0.14, -0.79
0.2 mass% MPS	89.99 (1.08) [c]	5.31, -4.78, 1.59, 1.68	73.84 (1.03) [f]	8.85, -8.67, 0.25, -1.61
0.4 mass% MPS	89.54 (0.58) [b, c]	5.24, -4.57, 1.83, 1.79	77.98 (1.15) [g]	7.97, -7.31, 0.15, -3.05

Values with the same letters are not statistically significant different (p<0.05)
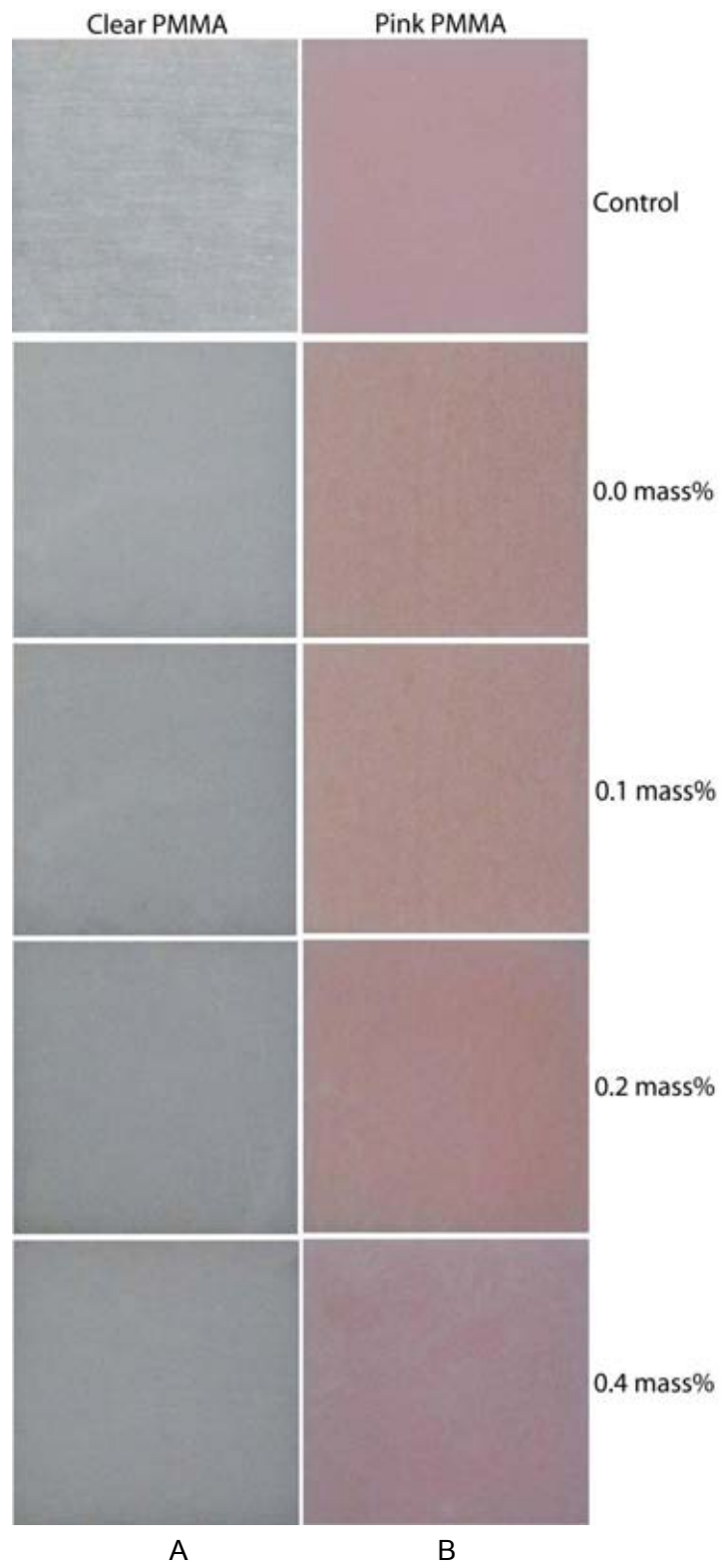
Figure 22 The opacity and color change of pink (A) and clear (B) PMMA specimens.

CHAPTER V

DISCUSSION AND CONCLUSION

Part 1: The effect of various types of silane coupling agent and silanization process (solutions of different polarity) on alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

The present study was conducted with an attempt to improve the mechanical properties of denture base polymer by adding alumina. The objective of this study was to evaluate the effect of the three silane coupling agents and the three different polar solutions on the mechanical properties of PMMA bonding to alumina plates with thermocycling challenge.

From the previous study, the study did not show completely positive results probably due to the lack of silanization [61]. Therefore, the effects of solubility parameters of the silane coupling agents and polarity of solutions for silanization of alumina were investigated. For application of adding alumina in a denture base polymer, alumina powder was used. However, alumina plates were alternatively investigated instead of alumina particles because it was easy and clear to evaluate the interface between alumina and PMMA.

There are various types of silane coupling agents available. In the part 1 of this study, MPS, APS and AAPS were selected based on their solubility parameters for PMMA bonding. The Hildebrand solubility parameters of PMMA, methylmethacrylate, MPS, APS and AAPS according to the manufacturer's information are 8.75 [77], 9.2 [78], 9.48, 9.86 and 10.24 respectively; the solubility parameters of MMA and MPS are the closest. This corresponded to the contact angle of alumina plate which silanized with MPS, the degree was smaller than that of the others. The result suggested that MPS had created high surface energy and could compatible with MMA than the other silanes.

Various types of solution have been suggested for silanization [9, 15]. Three solutions, ETH, ISP, and TOL, were selected in the present study based on their polarity and widely used in the previous studies [9,16,18]. It is essential to hydrolyze silane coupling agents in silanization, therefore, 70% ethanol aqueous solution was used. A

solution with a small polarity index, such as TOL (polarity index of 2.3) [79], is difficult to dissolve in water; therefore, TOL was used without water (solubility in water of TOL is 0.051%) [79]. ISP is 100% soluble in water, but was used without water in the present study to confirm the effect of water and polarity comparing ETH and TOL.

From the result of the part 1, the shear bond strengths of non- thermocyclings in all silanized groups were greater than that of the untreated condition. The bond strengths statistically decreased after thermocyclings except in untreated condition; however, the bond strengths in ETH, more than 5.0 MPa, were significantly greater than those of the other conditions. These strengths were not a great value, because the surface of alumina plate was relatively smooth (Ra was 0.18 μm).

Additionally, the highest bond strength was obtained from MPS and APS in ETH non-thermocycling, and the bond strength in ETH of all groups after thermocyclings were significantly greater than the other conditions. This might be attributed to the polar solution in silanization process of the ETH, which having the more positive charge of polar hydroxyl group, which could easily hydrolyze alkoxy group of silane. In addition, water is the important molecule to initiate the reaction. The water content in silane solution also affects the monolayer formation model by changing from continuous growth in low moisture to the island growth at high moisture [18,19]. Moreover, water can eliminate the improper orientation of aminosilanes which interrupts the complete forming of siloxane bond with the substrate surface [19]. The rate of hydrolysis and condensation of silane coupling agent also depends on the water content [7,18,19]. Thus, the ETH was effective in the hydrolysis reaction compared to ISP and TOL.

Among the three silanes, AAPS and APS were used without mixing with water, because these aminosilanes could be easily hydrolyzed by using moisture in the air. The rates of hydrolysis of the alkoxy groups are generally related to their steric bulk; CH_3O (MPS) > C_2H_5O (APS and AAPS) [65]. Moreover, AAPS has longer chain length than APS and has higher molecular weight than the MPS and APS. Thus, it could be hypothesized that the forming of silanol groups and siloxane bond seemed to be difficult to occur due to the steric hindrance effect.

According to the EDS and FTIR analysis in silanized groups, the alumina surface after THF washing and fracture surface where PMMA was removed after shear

bond test, the result of EDS analysis demonstrated that the silica element was still observed on the surface of alumina plate which demonstrated the existence of silanol groups. From FTIR analysis, the peak of Si-O-Si was shown. This confirmed the siloxane bond on the alumina surface. These findings suggested that the silane coupling agent created bond between PMMA and alumina. Determining the contact angle, the angle of all silanized condition were significant lower than in non-silanized alumina plate. These results confirmed that the silane coupling agent could improve surface wettability of the alumina plate. In addition, after shear bond test, the failure was hypothesized to occur within the physisorbed layer because this layer tends to form a weak boundary layer over the chemisorbed layer. The reduction in bond strength of all groups after thermocycling challenge in the same condition might be due to the hydrolysis of hydrogen bond in the physisorbed layer by hydrolytic attack [80]. Moreover, the stability of the Si-O-Al bond in thermocycling condition is easily cleaved by a polar molecule such as water to form an Al-OH bond resulting in reduces the bond strength between alumina and PMMA [81]. This was also confirmed by the reduction of all groups from thermocyclings.

The results of part 1 of this present study suggested that the alumina silanized with MPS and APS in ETH provided good and durable bond between PMMA and the alumina plate. The effective silanization potentially enhances the mechanical properties of alumina reinforced PMMA. The investigation on these applications is undergoing.

Part 2: The effect of silane coupling agent on alumina filler and mechanical properties of methacrylate base using alumina filler.

In the part 2 of this study, the flexural strength, flexural modulus, fracture toughness and two-body wear resistance of the PMMA containing alumina fillers treated with MPS have been used to investigate the adhesion between PMMA matrix and silanized alumina filler. Generally, there are various types of silane coupling agents available; however, MPS was selected based on its solubility parameters for PMMA bonding and good performance to alumina plate in the previous study [13, 77]. Additionally, the result in the part 1 also suggested that MPS in ETH provided the good

and durable bond between PMMA and the alumina plate. Spherical-shaped alumina was selected in order to avoid the interlocking effect from the other shapes of fillers. In using spherical filler, the fracture line will run through the least resistance plane during applying load. The silanization technique used in the present study followed the previous studies [8,34]. This wet technique was chosen because of easy manipulation and uniform coverage of filler.

Amounts of MPS used in part 2 were selected based on the Arkle's equation [17], which suggested the minimum amount of silane needed to create chemisorbed monolayer of MPS on alumina particle and double and four times of the minimum amount. The Arkle's equation is calculated based on the molecular distance between Si-O-Si; therefore, this equation may not truly represent but may be applicable for silanization of alumina. The intermolecular distances of Si-O and Al-O are 0.162 [82] and 0.185 nm [83], respectively; consequently, 0.1 mass% MPS might be a little bit excess to create only monolayer of MPS. However, the results of silicon deposition of alumina filler, the amount of Si of 0.1 mass% MPS before THF washing was slightly more than those of silanized alumina after THF washing. These findings suggested that the amount of 0.1 mass% for the alumina particle in the present study was adequate to create only chemisorbed monolayer of MPS. The detected amount of Si before THF washing did not proportionally increase with an increase of MPS. The reason of this finding was that EDS mainly analyzed the surface within a certain depth. If the alumina particle was analyzed using, for example, organic element analysis, the detected amounts of Si should be propositional to the MPS amounts for silanization [8]. Nevertheless, the detected Si amount before THF washing increased with an increase of MPS, and that after THF washing was almost constant regardless of MPS amount. These results indicated that the alumina surface of 0.2 and 0.4 mass% MPS consisted of not only chemisorbed but also physisorbed MPS.

Determining the effect of different amount of silane coupling agent in all amount of filler, the flexural strength of silanized groups were higher than No filler and 0.0 mass% MPS. This result agreed with the previous reports that only adding alumina did not improve mechanical properties of PMMA [61, 84]. According to the fracture surface of 0.0 mass% MPS, exposure of alumina filler were observed. The lack of interfacial

bonding between filler and matrix resin do not contribute to the improvement of mechanical properties but deteriorate. Regarding the MPS amounts of silica filler of a composite resin, the MPS amount did not significantly affect the flexural strength, [8] which agreed with the present results. However, the differences between solubility parameter of MPS (9.48) and urethane dimethacrylate (5.18) [85] used in the previous study was greater than between MPS and MMA (8.75) [78] in this study. Therefore, the failure layer in the previous study would occur in physisorbed or interpenetrating network layer [8] the same as 0.2 and 0.4 mass% MPS in this study, which also contained with physisorbed layer. This might attribute to the failure from flexural stress to occur in this weak layer and resulting in lower flexural strength. Moreover, silane absorbed on Al_2O_3 in aqueous solution was weaker than SiO_2 [80].

Additionally, the effect of different amount of filler was important. Considering the effect of amount of fillers in all amount of silane coupling agent, the flexural strengths of 10% alumina were significant difference from those of control, 30% and 50% alumina groups. The increase of amount of filler resulted in decrease the flexural strength. The reason might be from the increasing the amount of filler resulted in the reduction in the amount of resin matrix. This might affect the wetting of filler.

The alumina surface of 0.1 mass% MPS covered with monolayer of MPS had higher flexural properties as compared with the other silanized groups, but it was not significant. It could be hypothesized that only chemisorbed layer in 0.1 mass% MPS created covalent bond with alumina substrate and/or interpenetrated network with methacrylate based on solubility parameter [13,78]. This orientation will promote the strong bond between alumina particle and PMMA resulting in the higher flexural strength.

From the EDS analysis, there was Si on alumina surfaces in all silanized alumina filler groups. This confirmed that MPS was deposited on the alumina surface. Si in after THF washing groups was lower than non-THF washing groups. This attributed to the elimination of the excess amount by THF washing [8]. From Arkle's equation, the 0.1wt% of MPS in this study reflected the monolayer coverage which created only chemisorbed silane. This was confirmed by the same amount of Si on before and after THF washing. The excess amount over monolayer in 0.2 and 0.4 wt% of MPS resulted in physisorbed

silane which may be the susceptible layer for hydrolysis. In 0.0 mass% MPS group, the flexural properties were low due to no bonding between filler and resin matrix. This result was in agreement with the previous studies [9, 26, 62] which suggested that filler should be silanized effectively to reinforce PMMA.

From the result of TGA, in non-THF washing, the weight loss of 0.2, 0.4 mass% MPS group was almost 2-4 times higher than that of the 0.1 mass% MPS group. This might be from the 0.2, 0.4 mass% MPS had the excess of silane and forming the physisorbed which did not effectively bond with the alumina filler. While in 0.1 mass% MPS, it was expected to create chemisorbed monolayer on the filler surface [17]. In contrast with after THF washing, the percentage of weight loss of the 0.4 mass% MPS group was similar to the 0.1 and 0.2 mass% MPS groups. These might be confirmed that the THF washing could eliminate the physisorbed layer and remaining only chemisorbed layer on the alumina surface.

The flexural modulus represents the stiffness or rigidity of a material within the elastic range. From the result of this study, in 10% alumina reinforced PMMA, the modulus values were higher than non reinforced (no filler) and 0.0 mass% MPS group. The reasons might be from the well dispersed and good bonding to PMMA. The appropriate amount of silane caused effectively complete coating on the surface of alumina filler, increases the surface wettability and penetrates into the polymeric matrix, resulting in good adhesion and/or cohesion bonding between the materials. The excess amount over monolayer on filler resulted in less rigidity of the structure which may be attributed to the physisorbed silane [86]. In addition, in 30 and 50% alumina reinforcement, all of the modulus values were higher than No filler PMMA groups. The explanation might be from the additional of silanized fillers resulted in strengthening the whole structure due to the stiffness of alumina filler. In addition, the bonding between silanized alumina and PMMA was observed by SEM on the fracture surface. SEM images showed gap between the alumina filler and resin matrix in the 0.0 mass% MPS group. This is in agreement with several previous studies which suggested that using silane coupling agents as coating applications could promote adhesion between inorganic surfaces and polymeric molecules [8,34,87,88].

The fracture toughness represents the amount of stress required to propagate a preexisting flaw. From the results of this study, the fracture toughness of all alumina reinforced groups was higher than unreinforced group. These might be attributed to the chemical bond strength between silanized alumina filler and PMMA matrix which is higher than the yield stress or craze stress of the PMMA matrix. The bond strength is strong enough to endure the build-up of sufficient stress around the filler [89]. This is in agreement with a previous study which suggested that PMMA reinforcement with glass fibers and stainless steel wire resulted in increase fracture toughness of PMMA [89]. The author claimed that these increases were due to the mechanical interlocking which override the poor bonding effect of the fibers with the acrylic matrix [90]. However, these studies did not silanized the surface of reinforced fibers. The other study has investigated mechanical properties of polymer when added with 5 wt% nanophase alumina and 10 vol% multiwall carbon nanotubes (MWNT) composite. The result suggested that reinforced PMMA with 5 % nanophase alumina could increase in strain to failure, averaging over 28%; while reinforced with 10 vol % MWNT/alumina composite resulted in 4 times increase the fracture toughness over the neat PMMA [91]. Additionally, the fracture toughness of in 50 mass% alumina filler group was the highest and significant different from the other groups. The high percentage addition of silanized fillers resulted in strengthening the whole structure and limit crack propagation from the added silanized filler. In addition, the silane coupling agents coated on the filler in 50 mass% alumina filler were much more than the other groups due to the high amount of filler. These characteristic might be the main effect in providing reinforced resin with high fracture toughness. Generally, the resins have a shrinkage stress across the interface. Some of the silane coupling agent might modify the polymer properties in the stress interface resulted in increase of the toughness of the polymer [92].

Volume loss in 10 % alumina of all silanized filler reinforced PMMA groups was significantly lower than that of the non-silanized and control groups. But there were no significant effects of MPS amount on wear resistance except in 30% and 50% alumina. The volume loss of all groups was quite similar. The silane coupling agents affected this result due to the improvement in the dispersion of alumina filler and resulting in increase wear resistance. In 50% alumina, the filler was a half ratio with the PMMA matrix. During

wear testing, the antagonist could not drill through the alumina filler which was better in resisting the wear compared to unreinforced. Therefore; it resulted in the less of volume loss than the other groups. Additionally, SEM image showed the reducing of wear at the filler area and the exfoliation of the non-silanized alumina filler reinforced PMMA (Fig.20G). The PMMA containing non-silanized alumina filler is the weakest, since the chemical interaction between the filler and resin matrix is weak, only Van der Waals' force or hydrogen bonding. Bonds are much stronger, with the concomitant improvement in the mechanical properties, for PMMA containing silanized alumina filler [86]. This also reduces the incidence of filler exfoliation during abrasion. Comparing between reinforced and unreinforced filler in PMMA, the abrasive process might be interrupted from the alumina filler reinforcement which resulting in the reduction of wear in the resin matrix. The result supported the previous study which suggested that the addition of filler particles to the material can improve its wear resistance only if the particles are well-bonded to the resin matrix [86, 93].

Part 3: The effects of amount of sliane coupling agent of the alumina filler on color change of methacrylate-based polymer.

Determining the effect of amounts of silane coupling agent on the opacity of the pink and clear PMMA, the result in this study showed the opacities value of the No filler were significantly lower than the filler reinforced groups that in both of the pink and clear heat-polymerized PMMA groups. This result might be explained that the characteristic of alumina filler which is opaque [28] in nature affected the PMMA which reinforced with alumina filler to display the opacity when compared with the no alumina filler reinforced PMMA. In addition, in pink PMMA, the color changes of the specimens were lesser than those of clear PMMA. These result might be to the pink color pigment could camouflage the effect of the opacity of alumina filler. However, the amount of MPS did not influence the color change both in pink and clear PMMA. Additionally, in 0.1 mass% MPS group, which showed the best mechanical properties from the result of Part 1 and 2, the opacities of pink PMMA were significantly differences compared with the non-silanized

group but showed no change in clear PMMA. However, the ΔE values were still more than 3.3 which might be obviously different from conventional PMMA.

The results of this study may be beneficial in clinical application due to the reduction of denture damage by the improvement of the mechanical properties of PMMA by using alumina reinforcement. Additionally, the increase in the mechanical properties also strengthened the resins used in the fabrication of long-span provisional restorations. Another clinical situation that can benefit from the reinforcement of PMMA is the overdenture which usually breaks over, or adjacent to the abutments. However, there were several limitations to the present study, the mechanical properties evaluated in this study were only a limited view of the materials, and this *in-vitro* situation could not simulate the clinical condition. The additional of large amount alumina will dramatically increase the weight of the prosthesis. Future studies are suggested on fatigue properties and different shape and type of reinforced filler.

Conclusions:

Within the limitations of this in vitro study, it could be concluded that:

Part 1: The effect of various types of silane coupling agent and silanization process (solutions of different polarity) of alumina plate and thermocycling effects on the bond strength to methacrylate-based polymer.

1. The shear bond strengths of alumina plate silanized with MPS and APS in 70% ethanol aqueous solution with PMMA were 15.0 and 13.8 MPa, respectively in non-thermocyclings, which were statistically greater than the other conditions.

2. The shear bond strengths decreased after thermocyclings; however, the shear bond strengths in 70% ethanol aqueous solution of all silane, 5.0 to 8.5 MPa, were significantly greater than the other conditions.

3. EDS analysis indicated existence of Si on silanized alumina surface after THF washing and after the shear bond test, which suggested the effectiveness of silanization process in the present study.

Part 2: The effect of silane coupling agent on alumina filler and mechanical properties of methacrylate base using alumina filler.

1. The 0.1 mass% of MPS silanized on 10% alumina filler is adequate for improving the flexural properties.
2. All of the silanized alumina filler groups can improve the wear resistance of alumina reinforced methacrylate denture base.
3. The 50% silanized alumina reinforced PMMA results in the most increasing of fracture toughness.

Part 3: The effects of amount of sliane coupling agent of the alumina filler on color change of methacrylate-based polymer.

1. The alumina filler affected the opacity and color change of PMMA
2. The ΔE values of all groups were still more than 3.3 which might be not clinically acceptable.

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APPENDICES

APPENDICES

APPENDIX A

Surface Roughness of Alumina

One-Sample Kolmogorov-Smirnov Test

1=control, 2=pyranha, 3=503et,4=603et,5=903et,6=503tol,7=603tol,8=903tol,9=503 iso,10=603iso,11=903iso			ROUGHNES
1	N		12
	Normal Parameters(a,b)	Mean	.143642
		Std. Deviation	.0193196
	Most Extreme Differences	Absolute	.163
		Positive	.163
		Negative	-.115
	Kolmogorov-Smirnov Z		.564
	Asymp. Sig. (2-tailed)		.908
2	N		12
	Normal Parameters(a,b)	Mean	.186092
		Std. Deviation	.0089008
	Most Extreme Differences	Absolute	.176
		Positive	.176
		Negative	-.130
	Kolmogorov-Smirnov Z		.610
	Asymp. Sig. (2-tailed)		.850
3	N		12
	Normal Parameters(a,b)	Mean	.138525
		Std. Deviation	.0060705
	Most Extreme Differences	Absolute	.185
		Positive	.185
		Negative	-.144
	Kolmogorov-Smirnov Z		.640
	Asymp. Sig. (2-tailed)		.808
4	N		12
	Normal Parameters(a,b)	Mean	.138542

		Std. Deviation	.0143319
	Most Extreme Differences	Absolute	.115
		Positive	.115
		Negative	-.114
	Kolmogorov-Smirnov Z		.399
	Asymp. Sig. (2-tailed)		.997
5	N		12
	Normal Parameters(a,b)	Mean	.130642
		Std. Deviation	.0117493
	Most Extreme Differences	Absolute	.145
		Positive	.103
		Negative	-.145
	Kolmogorov-Smirnov Z		.501
	Asymp. Sig. (2-tailed)		.963
6	N		12
	Normal Parameters(a,b)	Mean	.131933
		Std. Deviation	.0139382
	Most Extreme Differences	Absolute	.307
		Positive	.307
		Negative	-.206
	Kolmogorov-Smirnov Z		1.065
	Asymp. Sig. (2-tailed)		.207
7	N		12
	Normal Parameters(a,b)	Mean	.129342
		Std. Deviation	.0050464
	Most Extreme Differences	Absolute	.212
		Positive	.212
		Negative	-.146
	Kolmogorov-Smirnov Z		.735
	Asymp. Sig. (2-tailed)		.653
8	N		12
	Normal Parameters(a,b)	Mean	.131375
		Std. Deviation	.0057173
	Most Extreme Differences	Absolute	.171
		Positive	.112
		Negative	-.171

	Kolmogorov-Smirnov Z		.593
	Asymp. Sig. (2-tailed)		.873
9	N		12
	Normal Parameters(a,b)	Mean	.136350
		Std. Deviation	.0060277
	Most Extreme Differences	Absolute	.210
		Positive	.170
		Negative	-.210
	Kolmogorov-Smirnov Z		.726
	Asymp. Sig. (2-tailed)		.667
10	N		12
	Normal Parameters(a,b)	Mean	.132683
		Std. Deviation	.0050468
	Most Extreme Differences	Absolute	.165
		Positive	.165
		Negative	-.114
	Kolmogorov-Smirnov Z		.573
	Asymp. Sig. (2-tailed)		.898
11	N		12
	Normal Parameters(a,b)	Mean	.134033
		Std. Deviation	.0068802
	Most Extreme Differences	Absolute	.135
		Positive	.105
		Negative	-.135
	Kolmogorov-Smirnov Z		.466
	Asymp. Sig. (2-tailed)		.982

a Test distribution is Normal.
b Calculated from data.

Test of Homogeneity of Variances

ROUGHNES

Levene Statistic	df1	df2	Sig.
3.244	10	121	.001

Robust Tests of Equality of Means

ROUGHNES

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	28.524	10	62.299	.000

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: ROUGHNES

	(I) 1=control, 2=pyranha, 3=503et, 4=603et,5=903et,6=503tol,7=603tol,8=903tol,9=503iso,10=603iso,11=903iso	(J) 1=control, 2=pyranha, 3=503et, 4=603et,5=903et,6=503tol,7=603tol,8=903tol,9=503iso,10=603iso,11=903iso	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tamhane	1	2	-.042450(*)	.0061405	.000	-.067495	-.017405
		3	.005117	.0058459	1.000	-.019701	.029934
		4	.005100	.0069441	1.000	-.021775	.031975
		5	.013000	.0065275	.970	-.012762	.038762
		6	.011708	.0068770	.998	-.014969	.038386
		7	.014300	.0057642	.793	-.010522	.039122
		8	.012267	.0058162	.956	-.012548	.037082
		9	.007292	.0058422	1.000	-.017525	.032108
		10	.010958	.0057642	.990	-.013864	.035781
		11	.009608	.0059202	.999	-.015233	.034449
	2	1	.042450(*)	.0061405	.000	.017405	.067495
		3	.047567(*)	.0031101	.000	.035439	.059694
		4	.047550(*)	.0048702	.000	.028373	.066727
		5	.055450(*)	.0042551	.000	.039009	.071891
		6	.054158(*)	.0047740	.000	.035417	.072900
		7	.056750(*)	.0029537	.000	.044998	.068502
		8	.054717(*)	.0030538	.000	.042736	.066698
		9	.049742(*)	.0031032	.000	.037633	.061851
		10	.053408(*)	.0029537	.000	.041657	.065160
		11	.052058(*)	.0032476	.000	.039529	.064588
	3	1	-.005117	.0058459	1.000	-.029934	.019701
		2	-.047567(*)	.0031101	.000	-.059694	-.035439
		4	-.000017	.0044931	1.000	-.018523	.018489
		5	.007883	.0038177	.956	-.007475	.023242
		6	.006592	.0043887	1.000	-.011426	.024610
		7	.009183(*)	.0022788	.032	.000432	.017935
		8	.007150	.0024073	.324	-.002053	.016353
		9	.002175	.0024696	1.000	-.007261	.011611

	10	.005842	.0022789	.632	-.002910	.014594
	11	.004492	.0026487	.998	-.005653	.014636
4	1	-.005100	.0069441	1.000	-.031975	.021775
	2	-.047550(*)	.0048702	.000	-.066727	-.028373
	3	.000017	.0044931	1.000	-.018489	.018523
	5	.007900	.0053499	1.000	-.012662	.028462
	6	.006608	.0057712	1.000	-.015446	.028663
	7	.009200	.0043863	.956	-.009225	.027625
	8	.007167	.0044543	1.000	-.011303	.025636
	9	.002192	.0044883	1.000	-.016309	.020693
	10	.005858	.0043863	1.000	-.012567	.024284
	11	.004508	.0045893	1.000	-.014118	.023135
5	1	-.013000	.0065275	.970	-.038762	.012762
	2	-.055450(*)	.0042551	.000	-.071891	-.039009
	3	-.007883	.0038177	.956	-.023242	.007475
	4	-.007900	.0053499	1.000	-.028462	.012662
	6	-.001292	.0052624	1.000	-.021487	.018904
	7	.001300	.0036913	1.000	-.013880	.016480
	8	-.000733	.0037720	1.000	-.016018	.014551
	9	-.005708	.0038120	1.000	-.021057	.009641
	10	-.002042	.0036914	1.000	-.017221	.013138
	11	-.003392	.0039305	1.000	-.018971	.012188
6	1	-.011708	.0068770	.998	-.038386	.014969
	2	-.054158(*)	.0047740	.000	-.072900	-.035417
	3	-.006592	.0043887	1.000	-.024610	.011426
	4	-.006608	.0057712	1.000	-.028663	.015446
	5	.001292	.0052624	1.000	-.018904	.021487
	7	.002592	.0042792	1.000	-.015334	.020518
	8	.000558	.0043490	1.000	-.017419	.018536
	9	-.004417	.0043837	1.000	-.022429	.013596
	10	-.000750	.0042793	1.000	-.018676	.017176
	11	-.002100	.0044871	1.000	-.020251	.016051
7	1	-.014300	.0057642	.793	-.039122	.010522
	2	-.056750(*)	.0029537	.000	-.068502	-.044998
	3	-.009183(*)	.0022788	.032	-.017935	-.000432
	4	-.009200	.0043863	.956	-.027625	.009225
	5	-.001300	.0036913	1.000	-.016480	.013880
	6	-.002592	.0042792	1.000	-.020518	.015334
	8	-.002033	.0022014	1.000	-.010465	.006398
	9	-.007008	.0022694	.262	-.015720	.001704
	10	-.003342	.0020603	.999	-.011214	.004531
	11	-.004692	.0024631	.983	-.014233	.004850
8	1	-.012267	.0058162	.956	-.037082	.012548
	2	-.054717(*)	.0030538	.000	-.066698	-.042736
	3	-.007150	.0024073	.324	-.016353	.002053
	4	-.007167	.0044543	1.000	-.025636	.011303
	5	.000733	.0037720	1.000	-.014551	.016018
	6	-.000558	.0043490	1.000	-.018536	.017419

	7	.002033	.0022014	1.000	-.006398	.010465
	9	-.004975	.0023983	.940	-.014143	.004193
	10	-.001308	.0022015	1.000	-.009740	.007123
	11	-.002658	.0025824	1.000	-.012576	.007259
9	1	-.007292	.0058422	1.000	-.032108	.017525
	2	-.049742(*)	.0031032	.000	-.061851	-.037633
	3	-.002175	.0024696	1.000	-.011611	.007261
	4	-.002192	.0044883	1.000	-.020693	.016309
	5	.005708	.0038120	1.000	-.009641	.021057
	6	.004417	.0043837	1.000	-.013596	.022429
	7	.007008	.0022694	.262	-.001704	.015720
	8	.004975	.0023983	.940	-.004193	.014143
	10	.003667	.0022694	.999	-.005046	.012379
	11	.002317	.0026406	1.000	-.007800	.012433
10	1	-.010958	.0057642	.990	-.035781	.013864
	2	-.053408(*)	.0029537	.000	-.065160	-.041657
	3	-.005842	.0022789	.632	-.014594	.002910
	4	-.005858	.0043863	1.000	-.024284	.012567
	5	.002042	.0036914	1.000	-.013138	.017221
	6	.000750	.0042793	1.000	-.017176	.018676
	7	.003342	.0020603	.999	-.004531	.011214
	8	.001308	.0022015	1.000	-.007123	.009740
	9	-.003667	.0022694	.999	-.012379	.005046
	11	-.001350	.0024632	1.000	-.010892	.008192
11	1	-.009608	.0059202	.999	-.034449	.015233
	2	-.052058(*)	.0032476	.000	-.064588	-.039529
	3	-.004492	.0026487	.998	-.014636	.005653
	4	-.004508	.0045893	1.000	-.023135	.014118
	5	.003392	.0039305	1.000	-.012188	.018971
	6	.002100	.0044871	1.000	-.016051	.020251
	7	.004692	.0024631	.983	-.004850	.014233
	8	.002658	.0025824	1.000	-.007259	.012576
	9	-.002317	.0026406	1.000	-.012433	.007800
	10	.001350	.0024632	1.000	-.008192	.010892

* The mean difference is significant at the .05 level.

Table of three-way ANOVA: the three main factors (silane coupling agents, solutions and thermocycling challenge) and their interactions were significant.

Tests of Between-Subjects Effects

Dependent Variable:shearbond

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2385.616[a]	17	140.330	75.171	.000
Intercept	5228.616	1	5228.616	2800.809	.000
silane	256.374	2	128.187	68.666	.000
solution	940.804	2	470.402	251.980	.000
thermo	936.717	1	936.717	501.771	.000
silane * solution	83.486	4	20.872	11.180	.000
silane * thermo	115.460	2	57.730	30.924	.000
solution * thermo	4.723	2	2.361	1.265	.286
silane * solution * thermo	48.052	4	12.013	6.435	.000
Error	235.220	126	1.867		
Total	7849.452	144			
Corrected Total	2620.836	143			

a. R Squared = .910 (Adjusted R Squared = .898)

Table of two-way ANOVA: the two main factors (amount of silane coupling agents and amount of alumina) and their interactions of Flexural strength, Flexural Modulus and Volume loss.

One-Sample Kolmogorov-Smirnov Test

SILANE	ALUMINA			FLEXURAL	MODULUS	VOL
0%	0%	N		10	10	10
		Normal Parameters(a,b)	Mean	95.1390	3.0940	.1600000
			Std. Deviation	12.13006	.23225	.02005232
		Most Extreme Differences	Absolute	.235	.210	.159
			Positive	.149	.210	.159
			Negative	-.235	-.176	-.136
		Kolmogorov-Smirnov Z		.744	.664	.503
		Asymp. Sig. (2-tailed)		.638	.769	.962
	10%	N		10	10	10
		Normal Parameters(a,b)	Mean	100.2520	3.1400	.0698900
			Std. Deviation	7.12266	.29166	.01283939
		Most Extreme Differences	Absolute	.235	.173	.199
			Positive	.235	.173	.166
			Negative	-.110	-.169	-.199
		Kolmogorov-Smirnov Z		.744	.546	.631
		Asymp. Sig. (2-tailed)		.636	.927	.821
	30%	N		10	10	10
		Normal Parameters(a,b)	Mean	87.5000	3.5920	.0598800
			Std. Deviation	9.93744	.46125	.01657406
		Most Extreme Differences	Absolute	.152	.192	.157
			Positive	.152	.179	.157
			Negative	-.102	-.192	-.129
		Kolmogorov-Smirnov Z		.480	.608	.496
		Asymp. Sig. (2-tailed)		.975	.853	.966
	50%	N		10	10	10
		Normal Parameters(a,b)	Mean	81.4300	3.4910	.0361500
			Std. Deviation	4.41885	.17508	.00950745
		Most Extreme Differences	Absolute	.108	.180	.152
			Positive	.083	.180	.120
			Negative	-.108	-.094	-.152
		Kolmogorov-Smirnov Z		.343	.568	.482
		Asymp. Sig. (2-tailed)		1.000	.904	.975
0.1	10%	N		10	10	10
		Normal Parameters(a,b)	Mean	117.79	3.8860	.037560

				90		0
			Std. Deviation	5.61365	.38945	.01078303
		Most Extreme Differences	Absolute	.323	.144	.162
			Positive	.323	.135	.110
			Negative	-.174	-.144	-.162
		Kolmogorov-Smirnov Z		1.023	.456	.512
		Asymp. Sig. (2-tailed)		.247	.985	.956
	30%	N		10	10	10
		Normal Parameters(a,b)	Mean	97.0760	3.8270	.0355600
			Std. Deviation	8.58143	.31896	.01674669
		Most Extreme Differences	Absolute	.186	.238	.135
			Positive	.129	.238	.135
			Negative	-.186	-.116	-.091
		Kolmogorov-Smirnov Z		.587	.754	.426
		Asymp. Sig. (2-tailed)		.881	.621	.994
	50%	N		10	10	10
		Normal Parameters(a,b)	Mean	96.8060	3.7260	.0256000
			Std. Deviation	3.60557	.10384	.00580460
		Most Extreme Differences	Absolute	.198	.137	.232
			Positive	.133	.137	.232
			Negative	-.198	-.102	-.159
		Kolmogorov-Smirnov Z		.627	.435	.735
		Asymp. Sig. (2-tailed)		.827	.992	.652
0.2	10%	N		10	10	10
		Normal Parameters(a,b)	Mean	108.7420	3.6550	.0385400
			Std. Deviation	7.91315	.22222	.00566906
		Most Extreme Differences	Absolute	.235	.173	.154
			Positive	.188	.173	.154
			Negative	-.235	-.103	-.117
		Kolmogorov-Smirnov Z		.745	.547	.486
		Asymp. Sig. (2-tailed)		.636	.925	.972
	30%	N		10	10	10
		Normal Parameters(a,b)	Mean	95.8080	3.1970	.0382000
			Std. Deviation	6.25036	.40324	.01504334
		Most Extreme Differences	Absolute	.184	.167	.230
			Positive	.184	.165	.230
			Negative	-.090	-.167	-.155
		Kolmogorov-Smirnov Z		.582	.528	.726
		Asymp. Sig. (2-tailed)		.887	.943	.668
	50%	N		10	10	10
		Normal Parameters(a,b)	Mean	94.3820	3.5450	.0278900
			Std. Deviation	3.24777	.09156	.00512563
		Most Extreme Differences	Absolute	.162	.222	.172
			Positive	.145	.150	.172
			Negative	-.162	-.222	-.093
		Kolmogorov-Smirnov Z		.513	.701	.545
		Asymp. Sig. (2-tailed)		.955	.709	.927
0.4	10%	N		10	10	10

			104.34 10	3.4650	.039030 0
	Normal Parameters(a,b)	Mean			
		Std. Deviation	9.8945 1	.37613	.005703 42
	Most Extreme Differences	Absolute	.361	.311	.178
		Positive	.361	.311	.178
		Negative	-.215	-.184	-.174
	Kolmogorov-Smirnov Z		1.142	.982	.562
	Asymp. Sig. (2-tailed)		.148	.290	.911
30%	N		10	10	10
	Normal Parameters(a,b)	Mean	94.966 0	3.5530	.036470 0
		Std. Deviation	4.3125 5	.36194	.007571 00
	Most Extreme Differences	Absolute	.174	.292	.204
		Positive	.119	.292	.204
		Negative	-.174	-.186	-.141
	Kolmogorov-Smirnov Z		.549	.924	.644
	Asymp. Sig. (2-tailed)		.924	.360	.801
50%	N		10	10	10
	Normal Parameters(a,b)	Mean	92.944 0	3.5490	.024940 0
		Std. Deviation	3.2842 6	.10908	.005614 31
	Most Extreme Differences	Absolute	.232	.105	.201
		Positive	.120	.105	.140
		Negative	-.232	-.098	-.201
	Kolmogorov-Smirnov Z		.735	.331	.636
	Asymp. Sig. (2-tailed)		.653	1.000	.814

a Test distribution is Normal.
b Calculated from data.

Flexural Strength

Tests of Between-Subjects Effects

Dependent Variable: FLEXURAL

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	9911.253[a]	11	901.023	20.529	.000
Intercept	1144743.188	1	1144743.188	26081.90	.000
ALUMINA	6256.122	2	3128.061	71.270	.000
SILANE	3173.420	3	1057.807	24.101	.000
ALUMINA * SILANE	481.711	6	80.285	1.829	.100
Error	4740.156	108	43.890		
Total	1159394.598	120			
Corrected Total	14651.409	119			

a. R Squared = .676 (Adjusted R Squared = .644)

Descriptives

FLEXURAL

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
0%	30	89.7273	10.77490	1.96722	85.7039	93.7507	73.13	117.40
0.1%	30	103.8937	11.69162	2.13459	99.5279	108.2594	80.83	132.76
0.2%	30	99.6440	8.83150	1.61240	96.3463	102.9417	87.29	118.62
0.4	30	97.4170	8.06256	1.47202	94.4064	100.4276	87.36	131.10
Total	120	97.6705	11.09599	1.01292	95.6648	99.6762	73.13	132.76

Test of Homogeneity of Variances

FLEXURAL

Levene Statistic	df1	df2	Sig.
3.208	3	116	.026

ANOVA

FLEXURAL

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3012.929	3	1004.310	9.718	.000
Within Groups	13021.88	126	103.348		
Total	16034.81	129			

Robust Tests of Equality of Means

FLEXURAL

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	10.691	3	106.960	.000

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: FLEXURAL

	(I) SILANE	(J) SILANE	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
Tukey HSD	0%	0.1%	-14.1663*	2.56837	.000	-20.8612	-7.4714
		0.2%	-9.9167*	2.56837	.001	-16.6116	-3.2218
		0.4	-7.6897*	2.56837	.017	-14.3846	-.9948
	0.1%	0%	14.1663*	2.56837	.000	7.4714	20.8612
		0.2%	4.2497	2.56837	.352	-2.4452	10.9446
		0.4	6.4767	2.56837	.062	-.2182	13.1716
	0.2%	0%	9.9167*	2.56837	.001	3.2218	16.6116
		0.1%	-4.2497	2.56837	.352	-10.9446	2.4452
		0.4	2.2270	2.56837	.822	-4.4679	8.9219
	0.4	0%	7.6897*	2.56837	.017	.9948	14.3846
		0.1%	-6.4767	2.56837	.062	-13.1716	.2182
		0.2%	-2.2270	2.56837	.822	-8.9219	4.4679
Dunnett T3	0%	0.1%	-14.1663*	2.90283	.000	-22.0611	-6.2716
		0.2%	-9.9167*	2.54358	.002	-16.8417	-2.9916
		0.4	-7.6897*	2.45699	.017	-14.3881	-.9913
	0.1%	0%	14.1663*	2.90283	.000	6.2716	22.0611
		0.2%	4.2497	2.67513	.518	-3.0423	11.5416
		0.4	6.4767	2.59293	.089	-.6033	13.5566
	0.2%	0%	9.9167*	2.54358	.002	2.9916	16.8417
		0.1%	-4.2497	2.67513	.518	-11.5416	3.0423
		0.4	2.2270	2.18327	.887	-3.7111	8.1651
	0.4	0%	7.6897*	2.45699	.017	.9913	14.3881
		0.1%	-6.4767	2.59293	.089	-13.5566	.6033
		0.2%	-2.2270	2.18327	.887	-8.1651	3.7111

*. The mean difference is significant at the .05 level.

Descriptives

FLEXURAL

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
10%	40	107.7835	9.97807	1.57767	104.5924	110.9746	91.39	132.76
30%	40	93.8375	8.20977	1.29808	91.2119	96.4631	73.13	108.53
50%	40	91.3905	6.94994	1.09888	89.1678	93.6132	73.18	101.10
Total	120	97.6705	11.09599	1.01292	95.6648	99.6762	73.13	132.76

Test of Homogeneity of Variances

FLEXURAL

Levene Statistic	df1	df2	Sig.
3.405	2	117	.037

ANOVA

FLEXURAL

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6315.278	3	2105.093	27.290	.000
Within Groups	9719.533	126	77.139		
Total	16034.81	129			

Robust Tests of Equality of Means

FLEXURAL

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	43.594	2	107.646	.000

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: FLEXURAL

	(I) ALUMINA	(J) ALUMINA	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	10%	30%	13.9460*	1.89413	.000	9.4495	18.4425
		50%	16.3930*	1.89413	.000	11.8965	20.8895
	30%	10%	-13.9460*	1.89413	.000	-18.4425	-9.4495
		50%	2.4470	1.89413	.403	-2.0495	6.9435
	50%	10%	-16.3930*	1.89413	.000	-20.8895	-11.8965
		30%	-2.4470	1.89413	.403	-6.9435	2.0495
Dunnett T3	10%	30%	13.9460*	2.04305	.000	8.9609	18.9311
		50%	16.3930*	1.92265	.000	11.6934	21.0926
	30%	10%	-13.9460*	2.04305	.000	-18.9311	-8.9609
		50%	2.4470	1.70075	.392	-1.7020	6.5960
	50%	10%	-16.3930*	1.92265	.000	-21.0926	-11.6934
		30%	-2.4470	1.70075	.392	-6.5960	1.7020

*. The mean difference is significant at the .05 level.

Between-Subjects Factors

		Value Label	N
ALUMINA	2	10%	40
	3	30%	40
	4	50%	40
SILANE	1	0%	30
	2	0.1%	30
	3	0.2%	30
	4	0.4	30

Flexural Modulus

Tests of Between-Subjects Effects

Dependent Variable: MODULUS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	5.368[a]	11	.488	5.336	.000
Intercept	1514.147	1	1514.147	16557.10	.000
SILANE	2.919	3	.973	10.638	.000
ALUMINA	.040	2	.020	.218	.804
SILANE * ALUMINA	2.409	6	.402	4.391	.001
Error	9.877	108	.091		
Total	1529.391	120			
Corrected Total	15.244	119			

a. R Squared = .352 (Adjusted R Squared = .286)

Descriptives

MODULUS

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	10	3.0940	.23225	.07344	2.9279	3.2601	2.75	3.44
2	10	3.1400	.29166	.09223	2.9314	3.3486	2.57	3.64
3	10	3.5920	.46125	.14586	3.2620	3.9220	2.83	4.44
4	10	3.4910	.17508	.05537	3.3658	3.6162	3.20	3.83
5	10	3.8860	.38945	.12315	3.6074	4.1646	3.13	4.43
6	10	3.8270	.31896	.10086	3.5988	4.0552	3.41	4.57
7	10	3.7260	.10384	.03284	3.6517	3.8003	3.57	3.87
8	10	3.6550	.22222	.07027	3.4960	3.8140	3.33	4.07
9	10	3.1970	.40324	.12752	2.9085	3.4855	2.51	3.91
10	10	3.5450	.09156	.02895	3.4795	3.6105	3.37	3.64
11	10	3.4650	.37613	.11894	3.1959	3.7341	2.93	4.41
12	10	3.5530	.36194	.11446	3.2941	3.8119	3.23	4.41
13	10	3.5490	.10908	.03449	3.4710	3.6270	3.34	3.70
Total	130	3.5169	.37008	.03246	3.4527	3.5811	2.51	4.57

Test of Homogeneity of Variances

MODULUS

Levene Statistic	df1	df2	Sig.
1.918	12	117	.039

ANOVA

MODULUS

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	7.306	12	.609	6.874	.000
Within Groups	10.362	117	.089		
Total	17.668	129			

Robust Tests of Equality of Means

MODULUS

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	6.874	12	76.435	.000

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: MODULUS
Tamhane

(I) GROUP	(J) GROUP	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.0460	.11790	1.000	-.5355	.4435
	3	-.4980	.16331	.510	-1.2198	.2238
	4	-.3970(*)	.09197	.037	-.7808	-.0132
	5	-.7920(*)	.14339	.005	-1.4090	-.1750
	6	-.7330(*)	.12477	.002	-1.2556	-.2104
	7	-.6320(*)	.08045	.000	-.9944	-.2696
	8	-.5610(*)	.10165	.002	-.9789	-.1431
	9	-.1030	.14715	1.000	-.7396	.5336
	10	-.4510(*)	.07894	.008	-.8134	-.0886
	11	-.3710	.13979	.759	-.9694	.2274
	12	-.4590	.13599	.272	-1.0379	.1199
	13	-.4550(*)	.08114	.007	-.8176	-.0924
2	1	.0460	.11790	1.000	-.4435	.5355
	3	-.4520	.17257	.779	-1.1882	.2842
	4	-.3510	.10757	.342	-.8134	.1114
	5	-.7460(*)	.15386	.012	-1.3885	-.1035
	6	-.6870(*)	.13668	.007	-1.2496	-.1244
	7	-.5860(*)	.09790	.006	-1.0419	-.1301
	8	-.5150(*)	.11595	.028	-.9984	-.0316
	9	-.0570	.15737	1.000	-.7167	.6027
	10	-.4050	.09667	.117	-.8623	.0523
	11	-.3250	.15051	.973	-.9514	.3014
	12	-.4130	.14699	.608	-1.0227	.1967
	13	-.4090	.09847	.108	-.8645	.0465

3	1	.4980	.16331	.510	-.2238	1.2198
	2	.4520	.17257	.779	-.2842	1.1882
	4	.1010	.15601	1.000	-.6192	.8212
	5	-.2940	.19090	1.000	-1.0830	.4950
	6	-.2350	.17734	1.000	-.9824	.5124
	7	-.1340	.14951	1.000	-.8639	.5959
	8	-.0630	.16191	1.000	-.7837	.6577
	9	.3950	.19374	.989	-.4041	1.1941
	10	.0470	.14871	1.000	-.6850	.7790
	11	.1270	.18821	1.000	-.6529	.9069
	12	.0390	.18541	1.000	-.7317	.8097
	13	.0430	.14988	1.000	-.6859	.7719
4	1	.3970(*)	.09197	.037	.0132	.7808
	2	.3510	.10757	.342	-.1114	.8134
	3	-.1010	.15601	1.000	-.8212	.6192
	5	-.3950	.13503	.618	-1.0027	.2127
	6	-.3360	.11506	.585	-.8376	.1656
	7	-.2350	.06437	.174	-.5122	.0422
	8	-.1640	.08946	.999	-.5358	.2078
	9	.2940	.13902	.988	-.3350	.9230
	10	-.0540	.06248	1.000	-.3285	.2205
	11	.0260	.13120	1.000	-.5612	.6132
	12	-.0620	.12714	1.000	-.6276	.5036
	13	-.0580	.06523	1.000	-.3369	.2209
5	1	.7920(*)	.14339	.005	.1750	1.4090
	2	.7460(*)	.15386	.012	.1035	1.3885
	3	.2940	.19090	1.000	-.4950	1.0830
	4	.3950	.13503	.618	-.2127	1.0027
	6	.0590	.15919	1.000	-.6004	.7184
	7	.1600	.12746	1.000	-.4535	.7735
	8	.2310	.14179	1.000	-.3833	.8453
	9	.6890	.17728	.081	-.0398	1.4178
	10	.3410	.12651	.831	-.2746	.9566
	11	.4210	.17121	.853	-.2829	1.1249
	12	.3330	.16813	.994	-.3588	1.0248
	13	.3370	.12789	.852	-.2756	.9496
6	1	.7330(*)	.12477	.002	.2104	1.2556
	2	.6870(*)	.13668	.007	.1244	1.2496
	3	.2350	.17734	1.000	-.5124	.9824
	4	.3360	.11506	.585	-.1656	.8376
	5	-.0590	.15919	1.000	-.7184	.6004
	7	.1010	.10607	1.000	-.3987	.6007
	8	.1720	.12293	1.000	-.3456	.6896
	9	.6300	.16258	.090	-.0454	1.3054
	10	.2820	.10494	.823	-.2194	.7834
	11	.3620	.15595	.924	-.2824	1.0064
	12	.2740	.15256	.999	-.3550	.9030
	13	.2780	.10660	.852	-.2211	.7771
7	1	.6320(*)	.08045	.000	.2696	.9944
	2	.5860(*)	.09790	.006	.1301	1.0419
	3	.1340	.14951	1.000	-.5959	.8639

	4	.2350	.06437	.174	-.0422	.5122
	5	-.1600	.12746	1.000	-.7735	.4535
	6	-.1010	.10607	1.000	-.6007	.3987
	8	.0710	.07757	1.000	-.2760	.4180
	9	.5290	.13168	.168	-.1068	1.1648
	10	.1810(*)	.04378	.049	.0005	.3615
	11	.2610	.12339	.992	-.3309	.8529
	12	.1730	.11907	1.000	-.3960	.7420
	13	.1770	.04762	.116	-.0188	.3728
8	1	.5610(*)	.10165	.002	.1431	.9789
	2	.5150(*)	.11595	.028	.0316	.9984
	3	.0630	.16191	1.000	-.6577	.7837
	4	.1640	.08946	.999	-.2078	.5358
	5	-.2310	.14179	1.000	-.8453	.3833
	6	-.1720	.12293	1.000	-.6896	.3456
	7	-.0710	.07757	1.000	-.4180	.2760
	9	.4580	.14560	.429	-.1763	1.0923
	10	.1100	.07600	1.000	-.2367	.4567
	11	.1900	.13815	1.000	-.4053	.7853
	12	.1020	.13431	1.000	-.4734	.6774
	13	.1060	.07828	1.000	-.2414	.4534
9	1	.1030	.14715	1.000	-.5336	.7396
	2	.0570	.15737	1.000	-.6027	.7167
	3	-.3950	.19374	.989	-1.1941	.4041
	4	-.2940	.13902	.988	-.9230	.3350
	5	-.6890	.17728	.081	-1.4178	.0398
	6	-.6300	.16258	.090	-1.3054	.0454
	7	-.5290	.13168	.168	-1.1648	.1068
	8	-.4580	.14560	.429	-1.0923	.1763
	10	-.3480	.13076	.850	-.9859	.2899
	11	-.2680	.17438	1.000	-.9854	.4494
	12	-.3560	.17135	.985	-1.0619	.3499
	13	-.3520	.13210	.839	-.9869	.2829
10	1	.4510(*)	.07894	.008	.0886	.8134
	2	.4050	.09667	.117	-.0523	.8623
	3	-.0470	.14871	1.000	-.7790	.6850
	4	.0540	.06248	1.000	-.2205	.3285
	5	-.3410	.12651	.831	-.9566	.2746
	6	-.2820	.10494	.823	-.7834	.2194
	7	-.1810(*)	.04378	.049	-.3615	-.0005
	8	-.1100	.07600	1.000	-.4567	.2367
	9	.3480	.13076	.850	-.2899	.9859
	11	.0800	.12242	1.000	-.5140	.6740
	12	-.0080	.11806	1.000	-.5790	.5630
	13	-.0040	.04504	1.000	-.1902	.1822
11	1	.3710	.13979	.759	-.2274	.9694
	2	.3250	.15051	.973	-.3014	.9514
	3	-.1270	.18821	1.000	-.9069	.6529
	4	-.0260	.13120	1.000	-.6132	.5612
	5	-.4210	.17121	.853	-1.1249	.2829
	6	-.3620	.15595	.924	-1.0064	.2824

	7	-.2610	.12339	.992	-.8529	.3309
	8	-.1900	.13815	1.000	-.7853	.4053
	9	.2680	.17438	1.000	-.4494	.9854
	10	-.0800	.12242	1.000	-.6740	.5140
	12	-.0880	.16507	1.000	-.7666	.5906
	13	-.0840	.12384	1.000	-.6751	.5071
12	1	.4590	.13599	.272	-.1199	1.0379
	2	.4130	.14699	.608	-.1967	1.0227
	3	-.0390	.18541	1.000	-.8097	.7317
	4	.0620	.12714	1.000	-.5036	.6276
	5	-.3330	.16813	.994	-1.0248	.3588
	6	-.2740	.15256	.999	-.9030	.3550
	7	-.1730	.11907	1.000	-.7420	.3960
	8	-.1020	.13431	1.000	-.6774	.4734
	9	.3560	.17135	.985	-.3499	1.0619
	10	.0080	.11806	1.000	-.5630	.5790
	11	.0880	.16507	1.000	-.5906	.7666
	13	.0040	.11954	1.000	-.5642	.5722
13	1	.4550(*)	.08114	.007	.0924	.8176
	2	.4090	.09847	.108	-.0465	.8645
	3	-.0430	.14988	1.000	-.7719	.6859
	4	.0580	.06523	1.000	-.2209	.3369
	5	-.3370	.12789	.852	-.9496	.2756
	6	-.2780	.10660	.852	-.7771	.2211
	7	-.1770	.04762	.116	-.3728	.0188
	8	-.1060	.07828	1.000	-.4534	.2414
	9	.3520	.13210	.839	-.2829	.9869
	10	.0040	.04504	1.000	-.1822	.1902
	11	.0840	.12384	1.000	-.5071	.6751
	12	-.0040	.11954	1.000	-.5722	.5642

* The mean difference is significant at the .05 level.

Volume loss

Descriptives

VOL

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	10	.16000000	.020052320	.006341101	.14565543	.17434457	.138000	.194400
2	10	.06989000	.012839388	.004060171	.06070525	.07907475	.054800	.087200
3	10	.05988000	.016574063	.005241179	.04802363	.07173637	.039400	.086600
4	10	.03615000	.009507453	.003006521	.02934878	.04295122	.019900	.051400
5	10	.03756000	.010783032	.003409894	.02984628	.04527372	.019300	.050800
6	10	.03556000	.016746688	.005295768	.02358014	.04753986	.010000	.064400
7	10	.02560000	.005804596	.001835574	.02144764	.02975236	.019800	.037200
8	10	.03854000	.005669058	.001792714	.03448460	.04259540	.031000	.047700
9	10	.03820000	.015043345	.004757123	.02743864	.04896136	.022900	.068300
10	10	.02789000	.005125633	.001620867	.02422334	.03155666	.021100	.037100
11	10	.03903000	.005703420	.001803580	.03495002	.04310998	.030900	.046500
12	10	.03647000	.007571005	.002394162	.03105403	.04188597	.027400	.048900
13	10	.02494000	.005614307	.001775400	.02092377	.02895623	.012400	.031000
Total	130	.04843923	.036296070	.003183376	.04214084	.05473762	.010000	.194400

Tests of Between-Subjects Effects

Dependent Variable: VOL

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.019[a]	11	.002	15.328	.000
Intercept	.184	1	.184	1614.613	.000
ALUMINA	.007	2	.003	30.253	.000
SILANE	.011	3	.004	30.774	.000
ALUMINA * SILANE	.002	6	.000	2.629	.020
Error	.012	108	.000		
Total	.215	120			
Corrected Total	.031	119			

a. R Squared = .610 (Adjusted R Squared = .570)

Test of Homogeneity of Variances

VOL

Levene Statistic	df1	df2	Sig.
4.729	12	117	.000

ANOVA

VOL

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.154	12	.013	94.351	.000
Within Groups	.016	117	.000		
Total	.170	129			

Robust Tests of Equality of Means

VOL

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	94.351	12	66.380	.000

a. Asymptotically F distributed.

Multiple Comparisons

Dependent Variable: VOL
Tamhane

(I) GROUP	(J) GROUP	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.09011000(*)	.007529578	.000	.05804550	.12217450
	3	.10012000(*)	.008226756	.000	.06606634	.13417366
	4	.12385000(*)	.007017743	.000	.09253214	.15516786
	5	.12244000(*)	.007199787	.000	.09095276	.15392724
	6	.12444000(*)	.008261641	.000	.09026718	.15861282
	7	.13440000(*)	.006601431	.000	.10288632	.16591368
	8	.12146000(*)	.006589642	.000	.08992534	.15299466
	9	.12180000(*)	.007927154	.000	.08870163	.15489837
	10	.13211000(*)	.006544980	.000	.10048629	.16373371
	11	.12097000(*)	.006592606	.000	.08944071	.15249929
	12	.12353000(*)	.006778021	.000	.09221764	.15484236
	13	.13506000(*)	.006584953	.000	.10351671	.16660329
2	1	-.09011000(*)	.007529578	.000	-.12217450	-.05804550
	3	.01001000	.006629853	1.000	-.01758342	.03760342
	4	.03374000(*)	.005052144	.000	.01261648	.05486352
	5	.03233000(*)	.005302110	.001	.01040716	.05425284
	6	.03433000(*)	.006673091	.006	.00652890	.06213110
	7	.04429000(*)	.004455819	.000	.02425434	.06432566
	8	.03135000(*)	.004438334	.001	.01131892	.05138108
	9	.03169000(*)	.006254215	.007	.00585735	.05752265
	10	.04200000(*)	.004371750	.000	.02196532	.06203468
	11	.03086000(*)	.004442734	.001	.01082797	.05089203
	12	.03342000(*)	.004713491	.000	.01310216	.05373784
	13	.04495000(*)	.004431369	.000	.02492013	.06497987
3	1	-.10012000(*)	.008226756	.000	-.13417366	-.06606634
	2	-.01001000	.006629853	1.000	-.03760342	.01758342

	4	.02373000	.006042278	.107	-.00242675	.04988675
	5	.02232000	.006252786	.189	-.00424787	.04888787
	6	.02432000	.007450846	.286	-.00630385	.05494385
	7	.03428000(*)	.005553313	.005	.00836152	.06019848
	8	.02134000	.005539294	.187	-.00459247	.04727247
	9	.02168000	.007078148	.411	-.00746587	.05082587
	10	.03199000(*)	.005486088	.010	.00599041	.05798959
	11	.02085000	.005542820	.215	-.00507881	.04677881
	12	.02341000	.005762115	.106	-.00245714	.04927714
	13	.03494000(*)	.005533715	.004	.00900155	.06087845
4	1	-.12385000(*)	.007017743	.000	-.15516786	-.09253214
	2	-.03374000(*)	.005052144	.000	-.05486352	-.01261648
	3	-.02373000	.006042278	.107	-.04988675	.00242675
	5	-.00141000	.004546047	1.000	-.02015325	.01733325
	6	.00059000	.006089690	1.000	-.02581466	.02699466
	7	.01055000	.003522570	.511	-.00455482	.02565482
	8	-.00239000	.003500427	1.000	-.01745326	.01267326
	9	-.00205000	.005627556	1.000	-.02605935	.02195935
	10	.00826000	.003415608	.907	-.00667159	.02319159
	11	-.00288000	.003506004	1.000	-.01795347	.01219347
	12	-.00032000	.003843329	1.000	-.01627617	.01563617
	13	.01121000	.003491591	.375	-.00383746	.02625746
5	1	-.12244000(*)	.007199787	.000	-.15392724	-.09095276
	2	-.03233000(*)	.005302110	.001	-.05425284	-.01040716
	3	-.02232000	.006252786	.189	-.04888787	.00424787
	4	.00141000	.004546047	1.000	-.01733325	.02015325
	6	.00200000	.006298614	1.000	-.02480131	.02880131
	7	.01196000	.003872559	.471	-.00497325	.02889325
	8	-.00098000	.003852428	1.000	-.01788908	.01592908
	9	-.00064000	.005852999	1.000	-.02520176	.02392176
	10	.00967000	.003775525	.848	-.00717205	.02651205
	11	-.00147000	.003857496	1.000	-.01838492	.01544492
	12	.00109000	.004166460	1.000	-.01643760	.01861760
	13	.01262000	.003844401	.358	-.00428017	.02952017
6	1	-.12444000(*)	.008261641	.000	-.15861282	-.09026718
	2	-.03433000(*)	.006673091	.006	-.06213110	-.00652890
	3	-.02432000	.007450846	.286	-.05494385	.00630385
	4	-.00059000	.006089690	1.000	-.02699466	.02581466
	5	-.00200000	.006298614	1.000	-.02880131	.02480131
	7	.00996000	.005604863	1.000	-.01623452	.03615452
	8	-.00298000	.005590973	1.000	-.02918902	.02322902
	9	-.00264000	.007118664	1.000	-.03196498	.02668498
	10	.00767000	.005538264	1.000	-.01860782	.03394782
	11	-.00347000	.005594467	1.000	-.02967524	.02273524
	12	-.00091000	.005811813	1.000	-.02704293	.02522293
	13	.01062000	.005585445	.999	-.01559520	.03683520
7	1	-.13440000(*)	.006601431	.000	-.16591368	-.10288632
	2	-.04429000(*)	.004455819	.000	-.06432566	-.02425434
	3	-.03428000(*)	.005553313	.005	-.06019848	-.00836152
	4	-.01055000	.003522570	.511	-.02565482	.00455482
	5	-.01196000	.003872559	.471	-.02889325	.00497325

	6	-.00996000	.005604863	1.000	-.03615452	.01623452
	8	-.01294000(*)	.002565766	.007	-.02348655	-.00239345
	9	-.01260000	.005098976	.907	-.03608308	.01088308
	10	-.00229000	.002448784	1.000	-.01238554	.00780554
	11	-.01343000(*)	.002573370	.005	-.02400728	-.00285272
	12	-.01087000	.003016843	.159	-.02343861	.00169861
	13	.00066000	.002553699	1.000	-.00983811	.01115811
8	1	-.12146000(*)	.006589642	.000	-.15299466	-.08992534
	2	-.03135000(*)	.004438334	.001	-.05138108	-.01131892
	3	-.02134000	.005539294	.187	-.04727247	.00459247
	4	.00239000	.003500427	1.000	-.01267326	.01745326
	5	.00098000	.003852428	1.000	-.01592908	.01788908
	6	.00298000	.005590973	1.000	-.02322902	.02918902
	7	.01294000(*)	.002565766	.007	.00239345	.02348655
	9	.00034000	.005083704	1.000	-.02315139	.02383139
	10	.01065000(*)	.002416823	.027	.00069668	.02060332
	11	-.00049000	.002542975	1.000	-.01094178	.00996178
	12	.00207000	.002990959	1.000	-.01042067	.01456067
	13	.01360000(*)	.002523067	.003	.00322993	.02397007
9	1	-.12180000(*)	.007927154	.000	-.15489837	-.08870163
	2	-.03169000(*)	.006254215	.007	-.05752265	-.00585735
	3	-.02168000	.007078148	.411	-.05082587	.00746587
	4	.00205000	.005627556	1.000	-.02195935	.02605935
	5	.00064000	.005852999	1.000	-.02392176	.02520176
	6	.00264000	.007118664	1.000	-.02668498	.03196498
	7	.01260000	.005098976	.907	-.01088308	.03608308
	8	-.00034000	.005083704	1.000	-.02383139	.02315139
	10	.01031000	.005025677	.995	-.01322959	.03384959
	11	-.00083000	.005087546	1.000	-.02431914	.02265914
	12	.00173000	.005325620	1.000	-.02180993	.02526993
	13	.01326000	.005077624	.843	-.01023519	.03675519
10	1	-.13211000(*)	.006544980	.000	-.16373371	-.10048629
	2	-.04200000(*)	.004371750	.000	-.06203468	-.02196532
	3	-.03199000(*)	.005486088	.010	-.05798959	-.00599041
	4	-.00826000	.003415608	.907	-.02319159	.00667159
	5	-.00967000	.003775525	.848	-.02651205	.00717205
	6	-.00767000	.005538264	1.000	-.03394782	.01860782
	7	.00229000	.002448784	1.000	-.00780554	.01238554
	8	-.01065000(*)	.002416823	.027	-.02060332	-.00069668
	9	-.01031000	.005025677	.995	-.03384959	.01322959
	11	-.01114000(*)	.002424894	.018	-.02112904	-.00115096
	12	-.00858000	.002891232	.512	-.02079908	.00363908
	13	.00295000	.002404008	1.000	-.00694689	.01284689
11	1	-.12097000(*)	.006592606	.000	-.15249929	-.08944071
	2	-.03086000(*)	.004442734	.001	-.05089203	-.01082797
	3	-.02085000	.005542820	.215	-.04677881	.00507881
	4	.00288000	.003506004	1.000	-.01219347	.01795347
	5	.00147000	.003857496	1.000	-.01544492	.01838492
	6	.00347000	.005594467	1.000	-.02273524	.02967524
	7	.01343000(*)	.002573370	.005	.00285272	.02400728
	8	.00049000	.002542975	1.000	-.00996178	.01094178

	9	.00083000	.005087546	1.000	-.02265914	.02431914
	10	.01114000(*)	.002424894	.018	.00115096	.02112904
	12	.00256000	.002997484	1.000	-.00995005	.01507005
	13	.01409000(*)	.002530799	.002	.00368783	.02449217
12	1	-.12353000(*)	.006778021	.000	-.15484236	-.09221764
	2	-.03342000(*)	.004713491	.000	-.05373784	-.01310216
	3	-.02341000	.005762115	.106	-.04927714	.00245714
	4	.00032000	.003843329	1.000	-.01563617	.01627617
	5	-.00109000	.004166460	1.000	-.01861760	.01643760
	6	.00091000	.005811813	1.000	-.02522293	.02704293
	7	.01087000	.003016843	.159	-.00169861	.02343861
	8	-.00207000	.002990959	1.000	-.01456067	.01042067
	9	-.00173000	.005325620	1.000	-.02526993	.02180993
	10	.00858000	.002891232	.512	-.00363908	.02079908
	11	-.00256000	.002997484	1.000	-.01507005	.00995005
	13	.01153000	.002980613	.095	-.00093032	.02399032
13	1	-.13506000(*)	.006584953	.000	-.16660329	-.10351671
	2	-.04495000(*)	.004431369	.000	-.06497987	-.02492013
	3	-.03494000(*)	.005533715	.004	-.06087845	-.00900155
	4	-.01121000	.003491591	.375	-.02625746	.00383746
	5	-.01262000	.003844401	.358	-.02952017	.00428017
	6	-.01062000	.005585445	.999	-.03683520	.01559520
	7	-.00066000	.002553699	1.000	-.01115811	.00983811
	8	-.01360000(*)	.002523067	.003	-.02397007	-.00322993
	9	-.01326000	.005077624	.843	-.03675519	.01023519
	10	-.00295000	.002404008	1.000	-.01284689	.00694689
	11	-.01409000(*)	.002530799	.002	-.02449217	-.00368783
	12	-.01153000	.002980613	.095	-.02399032	.00093032

* The mean difference is significant at the .05 level.

Fracture toughness

One-Sample Kolmogorov-Smirnov Test

1=control, 2= 10%,			KMAX
1	N		10
	Normal Parameters[a,b]	Mean	1.9350
		Std. Deviation	.44096
	Most Extreme Differences	Absolute	.186
		Positive	.186
		Negative	-.118
	Kolmogorov-Smirnov Z		.590
	Asymp. Sig. (2-tailed)		.878
2	N		10
	Normal Parameters[a,b]	Mean	2.3080
		Std. Deviation	.52057
	Most Extreme Differences	Absolute	.132
		Positive	.132
		Negative	-.109
	Kolmogorov-Smirnov Z		.416
	Asymp. Sig. (2-tailed)		.995
3	N		10
	Normal Parameters[a,b]	Mean	2.4000
		Std. Deviation	.28178
	Most Extreme Differences	Absolute	.172
		Positive	.172
		Negative	-.122
	Kolmogorov-Smirnov Z		.544
	Asymp. Sig. (2-tailed)		.929
4	N		10
	Normal Parameters[a,b]	Mean	2.6360
		Std. Deviation	.34510
	Most Extreme Differences	Absolute	.242
		Positive	.242
		Negative	-.126
	Kolmogorov-Smirnov Z		.764
	Asymp. Sig. (2-tailed)		.604

a. Test distribution is Normal.

b. Calculated from data.

Test of Homogeneity of Variances

KMAX

Levene Statistic	df1	df2	Sig.
.947	3	36	.428

ANOVA

KMAX

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2.546	3	.849	5.113	.005
Within Groups	5.975	36	.166		
Total	8.522	39			

Robust Tests of Equality of Means

KMAX

	Statistic[a]	df1	df2	Sig.
Brown-Forsythe	5.113	3	30.116	.006

a. Asymptotically F distributed.

KMAX

	1=control, 2= 10%, 3= 30%, 4= 50%	N	Subset for alpha = .05	
			1	2
Tukey HSD[a]	1	10	1.9350	
	2	10	2.3080	2.3080
	3	10	2.4000	2.4000
	4	10		2.6360
	Sig.		.069	.290

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 10.000.

Table of one-way ANOVA: the factors of color change (opacity).

Pink PMMA

One-Sample Kolmogorov-Smirnov Test

1=control, 2=No, 3=0.1, 4= 0.2, 5=0.4			opacity
1	N		12
	Normal Parameters[a]	Mean	79.6500
		Std. Deviation	1.13818
	Most Extreme Differences	Absolute	.148
		Positive	.105
		Negative	-.148
	Kolmogorov-Smirnov Z		.512
	Asymp. Sig. (2-tailed)		.956
2	N		12
	Normal Parameters[a]	Mean	93.1583
		Std. Deviation	.90900
	Most Extreme Differences	Absolute	.151
		Positive	.112
		Negative	-.151
	Kolmogorov-Smirnov Z		.524
	Asymp. Sig. (2-tailed)		.947
3	N		12
	Normal Parameters[a]	Mean	88.3500
		Std. Deviation	1.42287
	Most Extreme Differences	Absolute	.157
		Positive	.107
		Negative	-.157
	Kolmogorov-Smirnov Z		.545
	Asymp. Sig. (2-tailed)		.928

4	N		12
	Normal Parameters[a]	Mean	89.9917
		Std. Deviation	1.07826
	Most Extreme Differences	Absolute	.152
		Positive	.152
		Negative	-.123
	Kolmogorov-Smirnov Z		.527
	Asymp. Sig. (2-tailed)		.944
5	N		12
	Normal Parameters[a]	Mean	89.5417
		Std. Deviation	.58069
	Most Extreme Differences	Absolute	.195
		Positive	.195
		Negative	-.117
	Kolmogorov-Smirnov Z		.676
	Asymp. Sig. (2-tailed)		.750

a. Test distribution is Normal.

Levene's Test of Equality of Error Variances[a]

Dependent Variable:opacity

F	df1	df2	Sig.
1.078	4	55	.376

Tests the null hypothesis that the error variance
of the dependent variable is equal across groups.

a. Design: Intercept + group

Multiple Comparisons

Dependent Variable:opacity

	(I) 1=control, 2=No, 3=0.1, 4= 0.2, 5=0.4	(J) 1=control, 2=No, 3=0.1, 4= 0.2, 5=0.4	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	1	2	-13.5083*	.43383	.000	-14.7319	-12.2848
		3	-8.7000*	.43383	.000	-9.9235	-7.4765
		4	-10.3417*	.43383	.000	-11.5652	-9.1181
		5	-9.8917*	.43383	.000	-11.1152	-8.6681
	2	1	13.5083*	.43383	.000	12.2848	14.7319
		3	4.8083*	.43383	.000	3.5848	6.0319
		4	3.1667*	.43383	.000	1.9431	4.3902
		5	3.6167*	.43383	.000	2.3931	4.8402
	3	1	8.7000*	.43383	.000	7.4765	9.9235
		2	-4.8083*	.43383	.000	-6.0319	-3.5848
		4	-1.6417*	.43383	.003	-2.8652	-.4181
		5	-1.1917	.43383	.060	-2.4152	.0319
	4	1	10.3417*	.43383	.000	9.1181	11.5652
		2	-3.1667*	.43383	.000	-4.3902	-1.9431
		3	1.6417*	.43383	.003	.4181	2.8652
		5	.4500	.43383	.837	-.7735	1.6735
	5	1	9.8917*	.43383	.000	8.6681	11.1152
		2	-3.6167*	.43383	.000	-4.8402	-2.3931
		3	1.1917	.43383	.060	-.0319	2.4152
		4	-.4500	.43383	.837	-1.6735	.7735

Based on observed means.

 The error term is Mean Square(Error) = 1.129.

*. The mean difference is significant at the .05 level.

Clear PMMA

One-Sample Kolmogorov-Smirnov Test

1=clearcontrol, 2=no, 3=0.1, 4= 0.2, 5= 0.4			Opacity
1	N		12
	Normal Parameters[a]	Mean	38.6333
		Std. Deviation	3.27673
	Most Extreme Differences	Absolute	.171
		Positive	.171
		Negative	-.138
	Kolmogorov-Smirnov Z		.592
	Asymp. Sig. (2-tailed)		.875
2	N		12
	Normal Parameters[a]	Mean	79.0667
		Std. Deviation	1.31033
	Most Extreme Differences	Absolute	.184
		Positive	.110
		Negative	-.184
	Kolmogorov-Smirnov Z		.636
	Asymp. Sig. (2-tailed)		.813
3	N		12
	Normal Parameters[a]	Mean	79.6750
		Std. Deviation	1.37452
	Most Extreme Differences	Absolute	.134
		Positive	.134
		Negative	-.098
	Kolmogorov-Smirnov Z		.464
	Asymp. Sig. (2-tailed)		.982

4	N		12
	Normal Parameters[a]	Mean	73.8417
		Std. Deviation	1.03437
	Most Extreme Differences	Absolute	.149
		Positive	.149
		Negative	-.097
	Kolmogorov-Smirnov Z		.517
	Asymp. Sig. (2-tailed)		.952
5	N		12
	Normal Parameters[a]	Mean	77.9750
		Std. Deviation	1.15138
	Most Extreme Differences	Absolute	.189
		Positive	.189
		Negative	-.156
	Kolmogorov-Smirnov Z		.656
	Asymp. Sig. (2-tailed)		.783

a. Test distribution is Normal.

Test of Homogeneity of Variances

Opacity

Levene Statistic	df1	df2	Sig.
3.375	4	55	.015

Multiple Comparisons

Dependent Variable:Opacity

|	(I) 1=clear control, 2=no, 3=0.1, 4= 0.2, 5= 0.4	(J) 1=clear control, 2=no, 3=0.1, 4= 0.2, 5= 0.4	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tamhane	1	2	-40.43333*	1.01874	.000	-43.7916	-37.0751
		3	-41.04167*	1.02576	.000	-44.4102	-37.6732
		4	-35.20833*	.99192	.000	-38.5333	-31.8834
		5	-39.34167*	1.00261	.000	-42.6787	-36.0047
	2	1	40.43333*	1.01874	.000	37.0751	43.7916
		3	-.60833	.54820	.962	-2.3131	1.0965
		4	5.22500*	.48191	.000	3.7179	6.7321
		5	1.09167	.50354	.345	-.4767	2.6600
	3	1	41.04167*	1.02576	.000	37.6732	44.4102
		2	.60833	.54820	.962	-1.0965	2.3131
		4	5.83333*	.49659	.000	4.2764	7.3903
		5	1.70000*	.51761	.034	.0853	3.3147
	4	1	35.20833*	.99192	.000	31.8834	38.5333
		2	-5.22500*	.48191	.000	-6.7321	-3.7179
		3	-5.83333*	.49659	.000	-7.3903	-4.2764
		5	-4.13333*	.44680	.000	-5.5242	-2.7425
	5	1	39.34167*	1.00261	.000	36.0047	42.6787
		2	-1.09167	.50354	.345	-2.6600	.4767
		3	-1.70000*	.51761	.034	-3.3147	-.0853
		4	4.13333*	.44680	.000	2.7425	5.5242

APPENDIX B

Graph of TGA in unsilanized, silanized alumina filler and after THF washing groups.
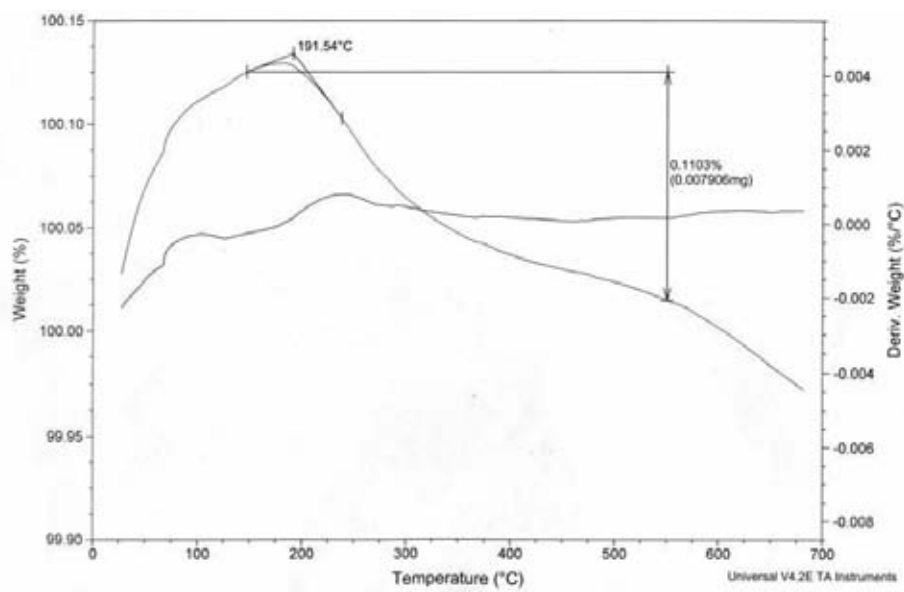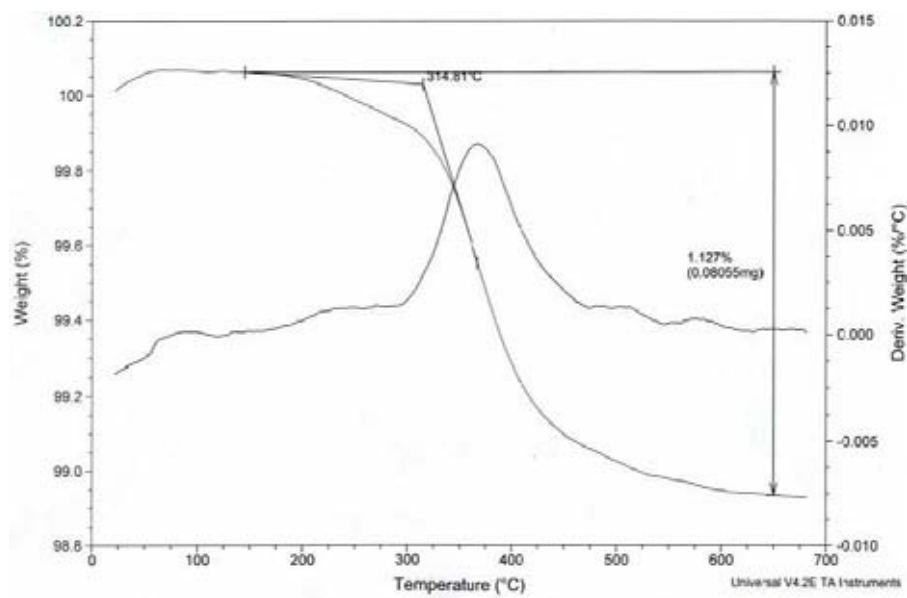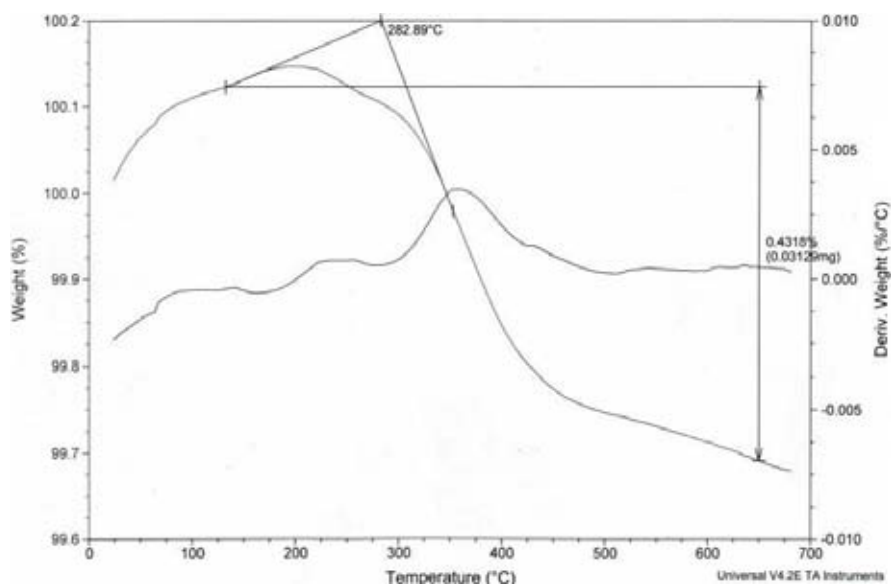

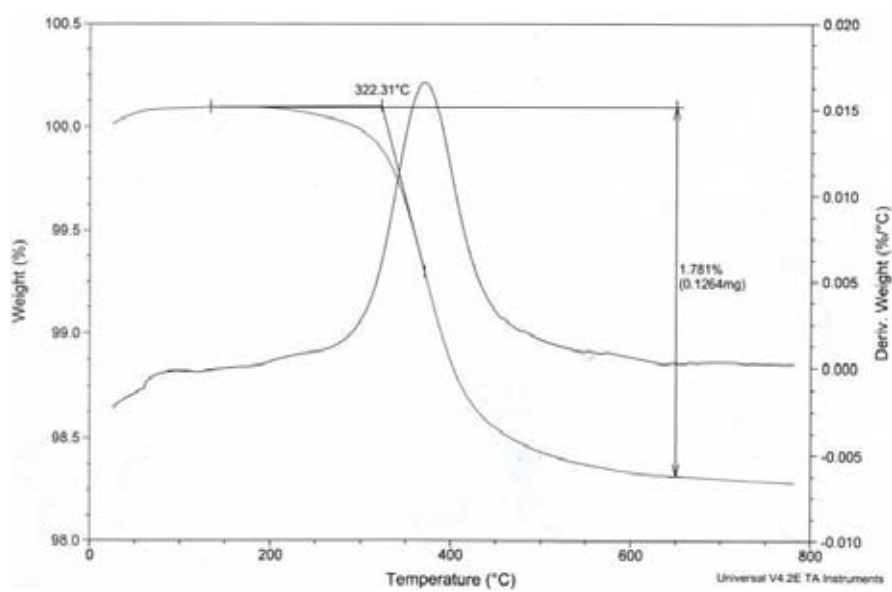Control group
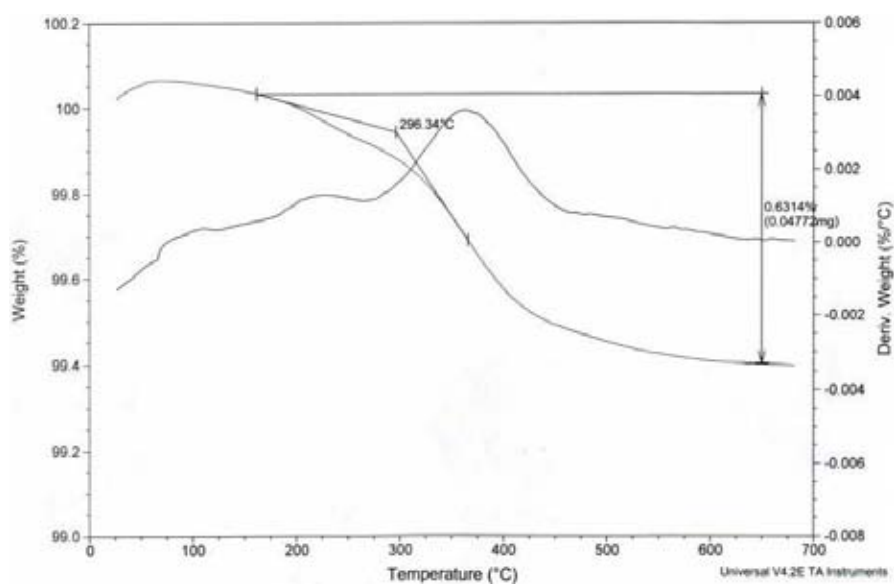
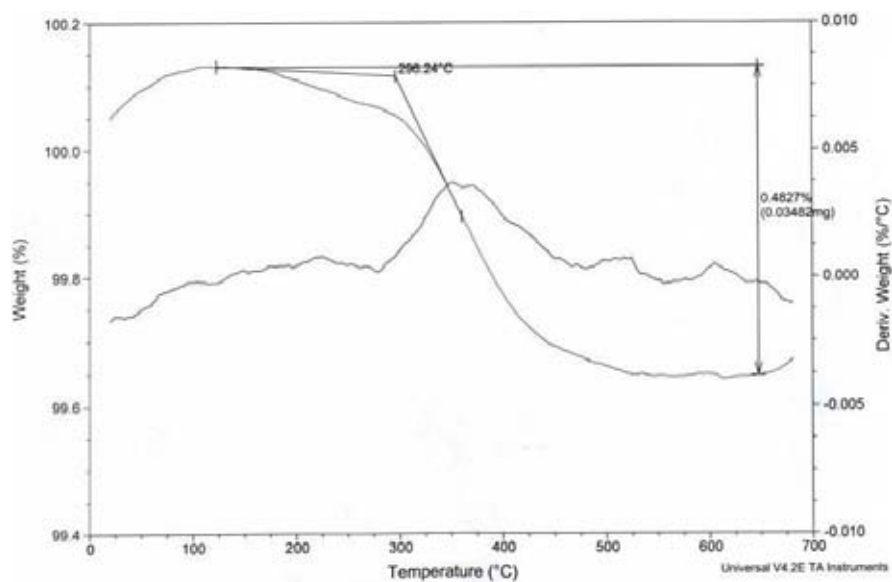0.1 mass% MPS group
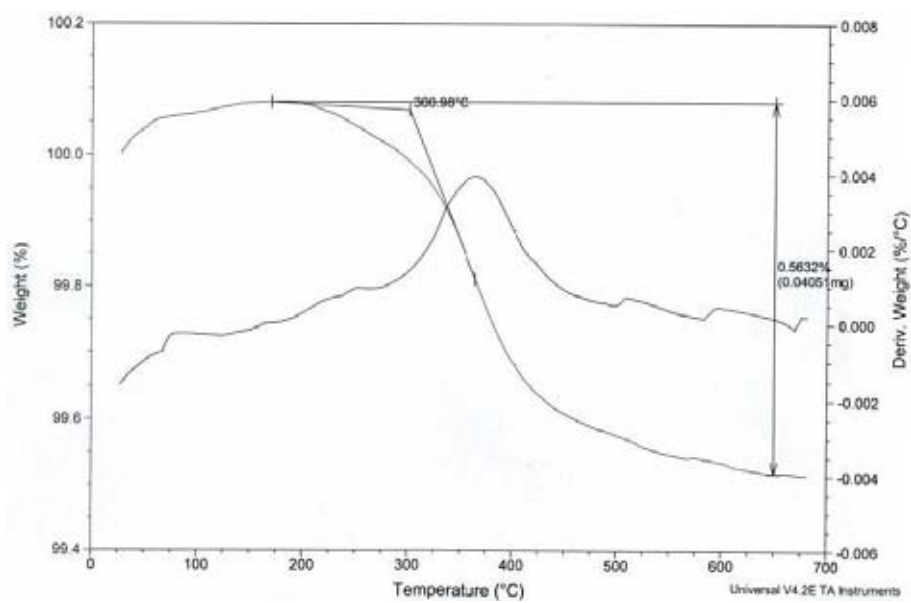
0.1 mass% MPS group after THF washing

0.2 mass% MPS group

0.2 mass% MPS group after THF washing

0.4 mass% MPS group

0.4 mass% MPS group after THF washing

VITA

Mr. Pisaisit Chaijareenont was born in Bangkok, Thailand on February 21, 1978. In 2001, he was conferred the Degree of Doctor of Dental Surgery (D.D.S.), from Faculty of Dentistry, Chiangmai University. After graduation, he worked as a lecturer in Prosthodontics Department, Faculty of Dentistry, Chiangmai University. In 2004, he started his post-graduated study for the Master of Science in Prosthodontics Program at the Faculty of Dentistry, Chulalongkorn University. After finished his Master of Science Program, he started his study for the Doctor of Philosophy in Oral Biology Program at the Faculty of Dentistry, Chulalongkorn University in 2007. At present, he works at the Department of Prosthodontics, Faculty of Dentistry, Chiangmai University.