ผลของสารควบคู่ไซเลนต่อความคงทนน้ำของคอมโพสิตเรซินที่มีซิลิกา หาด้วยคุณสมบัติดัดขวาง

นายแมนสรวง อักษรนุกิจ
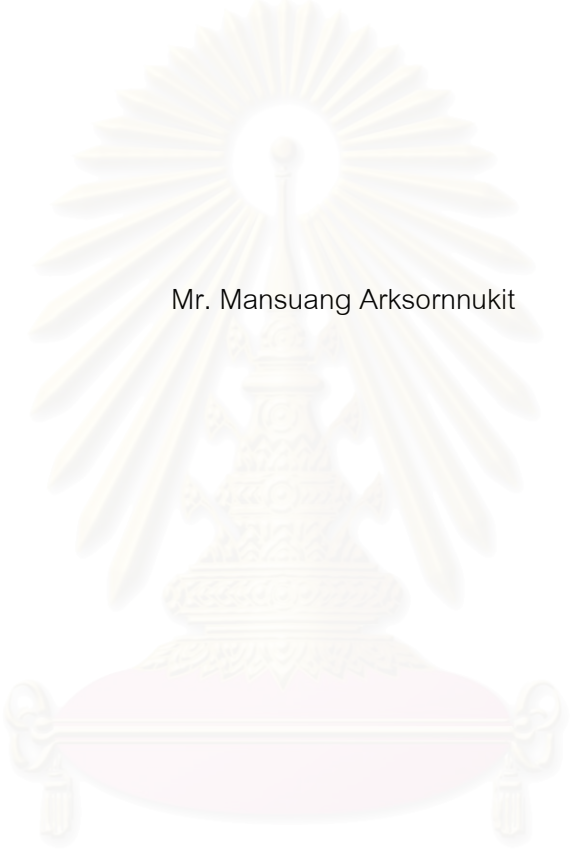
THE INFLUENCE OF SILANE COUPLING AGENT ON HYDROLYTIC DURABILITY OF

SILICA-CONTAINED COMPOSITE RESIN DETERMINED BY FLEXURAL PROPERTIES

Mr. Mansuang Arksornnukit

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Thesis Title   THE INFLUENCE OF SILANE COUPLING AGENT ON HYDROLYTIC
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By   Mansuang Arksornnukit

Program in   Oral Biology

Thesis Advisor   Associate Professor Dr. Prasit Pavasant, D.D.S., Ph.D.

Thesis Co-advisor   Associate Professor Dr. Hidekazu Takahashi, D.D.S., Ph.D.

Accepted by the Faculty of Dentistry, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Doctor's Degree

.... Dean of the Faculty of Dentistry

(Associate Professor Surasith Kiatpongsan, D.D.S., M.S.)

THESIS COMMITTEE

.... Chairman

(Piyamas Sumrejkanchanakij, D.D.S., Ph.D.)

.... Thesis Advisor

(Associate Professor Dr. Prasit Pavasant, D.D.S., Ph.D.)

.... Thesis Co-advisor

(Associate Professor Dr. Hidekazu Takahashi, D.D.S., Ph.D.)

.... Member

(Associate Professor Ratana Serinirach, D.D.S., Ph.D.)

.... Member

(Assistant Professor Prarom Salimee. D.D.S., Ph.D.)

.... Member

(Orapin Komin, D.D.S., Ph.D.)

แมนสรวง อักษรนุกิจ : ผลของสารควบคู่ไซเลนต่อความคงทนน้ำของคอมโพสิตเรซินที่มี
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คุณสมบัติเชิงกลที่ดีและความคงทนต่อน้ำของคอมโพสิตได้จากซิลิกาที่มีการเคลือบสาร
ควบคู่บนผิว การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาผลของปริมาณสารควบคู่ไซเลน ความร้อนที่ใช้ใน
ขบวนการเคลือบผิวและ pH ของสารละลายที่ใช้ในขั้นตอนการเคลือบผิว คุณสมบัติดัดขวางหาได้จาก
การเตรียมชิ้นงานและทดสอบตามมาตรฐาน ISO 4049 การทดสอบความคงทนของน้ำหาโดยคุณสมบัติ
ดัดขวางของชิ้นงานภายหลังการนำชิ้นงานไปไว้ใน Soxhlet's extractor การศึกษานี้ยังได้ใช้
กระบวนการวิเคราะห์ต่าง ๆ เช่น Organic Elemental Analysis, Fourier Transform Infrared
Spectroscopy, Thermogravimetric analysis และ Differential Scanning Colorimeter ในการวิเคราะห์หา
ปริมาณและคุณสมบัติของชั้นเคลือบผิวร่วมกับการวิเคราะห์จากกล้องจุลทรรศน์ชนิดส่องกราดของผิว
ด้านแตก ผลการศึกษาพบว่าการมีสารเคลือบควบคู่ไซเลนเคลือบบนผิวซิลิกาปริมาณต่าง ๆ ไม่มีผล
อย่างมีนัยสำคัญต่อคุณสมบัติดัดขวางและความคงทนต่อน้ำ ผลของ pH ของสารละลายที่ใช้ในขั้นตอน
การเคลือบผิวก็ไม่มีผลแตกต่างอย่างมีนัยสำคัญเช่นกัน ขณะที่ความร้อนที่ใช้ในการทำให้ซิลิกาแห้งมี
ผลต่อคุณสมบัติดัดขวางและความต้านทานต่อน้ำอย่างมีนัยสำคัญ จากผลการศึกษาครั้งนี้สามารถสรุป
ได้ว่า ปริมาณสารควบคู่ไซเลน และpH ของสารละลายที่ใช้ในการเคลือบผิวไม่มีผลต่อคุณสมบัติดัด
ขวางและความคงทนต่อน้ำในภาพรวมแต่เมื่อวิเคราะห์ดูแล้วพบว่าปริมาณสารควบคู่ไซเลนปริมาณ
หนึ่ง ซึ่งไม่มากหรือน้อยเกินไปสามารถทำให้คุณสมบัติดัดขวางและความคงทนของน้ำสูงกว่า การใช้
ความร้อนที่อุณหภูมิต่ำกว่า 80°C ในการทำให้ซิลิกาแห้งภายหลังการเคลือบผิวเป็นเวลา 3 ชั่วโมงมีผล
ทำให้คอมโพสิตมีความคงทนต่อน้ำสูงและมีคุณสมบัติดัดขวางดีขึ้น

สาขาวิชา	ชีววิทยาช่องปาก	ลายมือชื่อนิสิต……………………………………..
ปีการศึกษา	2546	ลายมือชื่ออาจารย์ที่ปรึกษา………………………....
		ลายมือชื่ออาจารย์ที่ปรึกษาร่วม……………..……

Using silanated filler in making dental resin composite results in the superior performance in both mechanical properties and durability of composite. The objectives of this study were to elucidate the effect of amount of silane coupling agent, gamma-methacryloxypropyltrimethoxysilane, the heat used in silanation process and pH of silanating solution on flexural properties and hydrolytic durability of composite. Flexural properties were obtained from specimens' preparation following ISO 4049:2000 and hydrolytic durability was obtained from subjecting the specimens in Soxhlet's extractor. An organic elemental analysis, a Fourier transform infrared spectroscopy, a thermogravimetric analysis and a differential scanning colorimeter accompanied with a scanning electron microscope were utilized as the analyzing tools to understand the characteristics of the silane coupling agent on silica surface. Flexural properties of composite were fairly affected by the amount of silane providing that certain amount existed on the filler surface. Meanwhile, the flexural properties and hydrolytic durability were significantly depended upon the temperature used in drying the filler. Unlike, the heating effect, pH also showed the same trend as the effect of amount. The results were drawn from statistic analysis at $p < 0.05$. It was concluded that silanation of filler is a prerequisite for superior performance of composite with hydrolytic stability. The amount of silane coupling agent covering filler and pH of silanating solution are not strongly affected the flexural properties and hydrolytic durability. The application of heating less than 80ºC in drying filler for 3 hours resulted in better flexural properties and more hydrolytic durable composite.

Field of Study	Oral Biology	Student's signature…………………………...
Academic year	2003	Advisor's signature…………………………..
		Co-Advisor's signature…………………………

ACKNOWLEDGEMENT

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ABBREVIATIONS

BisGMA	2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)]phenylpropane
UDMA	1,6-bis(methacryloxy-2-methoxycarbomylamino)-2,4,4-trimethoxylhexane
TEGDMA	Triethylene glycol dimethacrylate
γ-MPTS	Gamma-methacryloxypropyltrimethoxysilane
THF	Tetrahydrofurane
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric analysis
DCS	Differential scanning colorimetry
GPC	Gel permeation chromatography
DRIFT	Diffuse reflectance infrared fourier transform spectroscopy

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Composite, in general, is a material containing two or more integrated materials (constituents or phases), which each material keeping its own identity. Normally, combination of the materials serves to rectify weakness possessed by each constituent when it exists alone.

Composite resin has been extensively used in dentistry because of its esthetic properties; tooth colored like material. Resin system first introduced and used in dentistry was based on methyl methacrylate technology around 1940's. But the first generation of this polymer was not so successful due to the unacceptable properties; polymerization shrinkage, low wear resistance, marginal leakage and discoloration. The first development of dental composite came from the discovery of Bowen in 1963[1] which he joined each end of bisphenol-A molecule with a glycidyl methacrylate molecule resulting in BisGMA molecule. This BisGMA posseses the hardening mechanism so called polymerization of methyl methacrylate and the stiffness of benzene ring from Bisphenol-A molecule. In addition, the introduction of acid etching technology for enamel bonding by Buonocore had made composite one of the forerunning developing field in questing for a more durable and esthetic material.

Dental composite contains three main components: resin matrix or polymer matrix, filler particles and a coupling agent. In addition to the main component, some small trace amount of activator-initiator and retarder were incorporated into the main components depended upon the polymerization system of the composite resin. Moreover, different pigments were added to the main component to improve the esthetic property of composite resin.

Resin Matrix:

BisGMA, 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)]phenylpropane, is widely used as a base monomer in polymeric dental materials, e.g. restorative composites, adhesives and prophylactic sealants. This monomer, which also is used as a commercial vinyl ester matrix monomer for structural composites, is synthesized by reacting glycidyl methacrylate with bisphenol A, or alternatively, by reacting the diglycidyl ether of bisphenol A and methacrylic acid.[1] The structure of the major product of these addition reactions, assigned the acronym BisGMA is shown below.
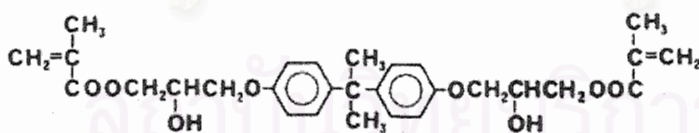
Fig 1.1 Chemical structure of BisGMA

Advantages of using BisGMA over smaller-sized dental monomers, such as methyl methacrylate, include lower volatility and diffusivity into tissue and the formation of higher moduli polymers with less volume contraction.[2] These desirable properties of BisGMA are partially negated by its relatively high viscosity and low vinyl conversion under ambient polymerization conditions. To overcome these deficiencies, a less viscous monomer is needed as a diluent comonomer, e.g. triethylene glycol dimethacrylate (TEGDMA) is frequently used to achieve a dental resin of workable viscosity. Unfortunately, the addition of smaller-sized diluent comonomers such as TEGDMA, while increasing vinyl conversion, also increases polymerization shrinkage and contributes to the development of concomitant stress sites in the polymeric dental composites and at the interfaces with tooth structure, resulting in interfacial gaps that can promote microleakage. However, the relatively high hydrophilicity and penetrability to tissues of TEGDMA raises biocompatibility issues, and recent studies have suggested that TEGDMA should be replaced by larger, more hydrophobic and biocompatible monomers.[3]
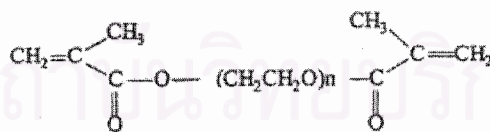
n=1: Ethylene glycol dimethacrylate (EGDMA), n=2: Diethylene glycol dimethacrylate (DEGDMA), n=3: Triethylene glycol dimethacrylate (TEGDMA)

Fig 1.2 Chemical structure of TEGDMA.

Other resin composites contain urethane dimethacrylate, 1,6-bis(methacryloxy-2-thoxycarbonylamino)-2,4,4-trimethoxylhexane (UDMA). The UDMA-based resins have recently been increasingly used as restorative materials. This monomer has been used alone or in combination with other monomer such as BisGMA and TEGDMA. The advantages of UDMA have been reported to be lower viscosity and a greater flexibility of the urethane linkage, which may improve the toughness of resin composites based on this monomer. However, a general difference between resin composites based on UDMA or other urethane dimethacrylates and conventional BisGMA-based resin composites is very hard to deduce from existing in vitro and in vivo studies. The reason is that difference caused by dissimilar monomer system is camouflaged by the fact that the materials differ in many other aspects, for example, type and amount of filler, type and amount of initiators, silanation of the filler particles, and the effects of which may be predominant for the properties than the nature of the copolymer. This, however, does not imply that the choices of monomer system are significant. Another possible reason may be the awareness of estrogenic effect from the bisphenol A derivative such as BisGMA[4] Therefore, UDMA at this moment is more acceptable than BisGMA in terms of safety.

Urethane dimethacrylate (UDMA)
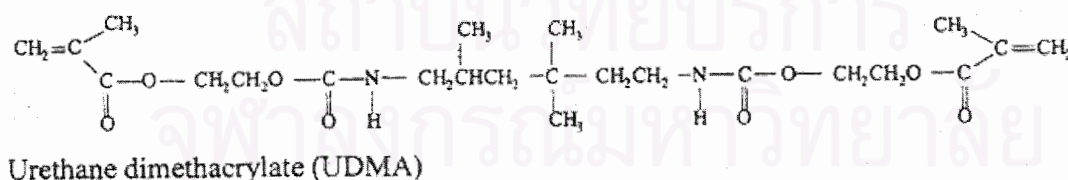
Fig 1.3 Chemical structure of UDMA.

Filler:

Filler is used to reduce the polymerization shrinkage of the composite and to strengthen the composite resin. Mostly, fillers are glass in nature such as amorphous silica, borosilicate glass, lithium or barium aluminum silicate, strontium or zinc glass and quartz. Fillers varies from size and shape; spherical, irregular etc. Therefore, fillers can be used in classification of composite by type, shape and size used to make composite.

Filler is used to control the viscosity of the composite resin. In order to achieve the clinical consistency, the various amounts of filler are incorporated into the matrix resin. This varied from 25-70% by volume and 38-90% by weight. The more filler added, the higher consistency of the composite resulted.

Extensive studies were performed to elucidate the role of fillers to the mechanical properties of composite resin. Li et al[5] studied the effect of filler content and size on properties of composites. They found that the increase in filler levels resulted in the increase in hardness, compressive strength, stiffness and the decrease in water sorption. Ferracane et al[6] demonstrated that fillers used in composite formulation appeared to play a major role in mechanical properties. Later Braem and his group[7] revealed the exponential regression equation to denote the mechanical properties of composite as a function of the volumetric filler fraction.

Regarding to the type of filler, Calais and Soderholm[8] compared three types of filler; barium glass, quartz, and porous silica. They found that barium glass was more susceptible to hydrolytic degradation than two other fillers. Comparing to quartz, Tarumi[9] also confirmed the hydrolytic instability of barium glass filler when stored in water.

Miyasaka[10] conducted extensive evaluation of the binary system of hybrid fillers from four irregular fillers, five spherical fillers and a microfiller. The results showed that the strength for the hybrid of irregular and spherical fillers tended to increase as the size of the component fillers decreased. The strength for the hybrid of the same shape fillers also increased as the size of the fillers decreased. Later Miyasaka and Yoshida[11] studied the effect of binary and ternary filler mixtures on the mechanical properties of composite resins. They concluded that the compressive strength of the microfilled ternary fillers increased with the decrease in the macrofiller size and with the increase in the mixing ratio of filler and matrix resin. A large diametral tensile strength was found in several microfilled ternary mixtures containing different shaped macrofillers. This can be concluded that the mechanical properties of composite resin especially strength depends upon the type, the amount, the size of fillers and mixing ratio.

In commercially available products of composite resins, they are varying in types, shapes and sizes of fillers used in the composite resin formulation. Therefore, it is worthy to understand the nature behavior of fillers in composite resin. But it is not within our scope of this study.

Silane Coupling Agent:[12]

Concept of bonding of organic polymers to inorganic surfaces has long been a familiar operation such as the protection coatings on metals. Careful preparation of glass-resin bonds under dry conditions did not produce more water-resistance composite. Bonding resin to fresh glass surfaces always fractured in liquid resin before polymerization and could not withstand the action of water. The interface between such dissimilar materials as an organic polymer and a mineral did not allow the formation of a water-resistance bond.

The concept that two dissimilar materials may be held together by a third intermediate material as coupling agent was used by Plato[12] to explain how a universe made up of four elements; earth, air, fire, water, could exist as homogeneous whole.

It is not possible for two things to be fairly united without a third, for they need a bond between them which shall join them both, that as the first is to the middle, so is the middle to the last, then since the middle becomes the first and the last, and the last and the first both become middle, of necessity, all will come to be the same, and being with one another, all will be unity.

Because organofunctional silanes are hybrids of silica and of organic materials related to resins, it is not surprising that they were utilized as coupling agents to improve bonding of organic resins to mineral surfaces. Modification of the interface between an organic polymer and an inorganic substrate may have been beneficial results in composite manufacture. Silane coupling agents should be defined as materials that improve the chemical resistance especially to water of the bond across the interface.

Silane coupling agent was first report in 1947 by Ralph K. Witt et al. of John Hopkins University in confidential report to the Navy Bureau of Ordnance. They observed that alkyltriethoxysilane on glass fibers gave polyester composites with twice strength of those where the glass was treated with ethyltrichlorosilane.

Organofunctional silanes may be used as adhesion promoters between organic polymers and mineral substrates under a variety of circumstances. The silane adhesion promoter or coupling agent may function as a finish (or surface modifier), a primer (or size) or an adhesive, depending on the thickness of the bonding material at the interface.

A finish or surface modifier is only a monomolecular layer, but in practice it may be several monolayers thick. The material functions as a chemical surface modifier without contributing any mechanical film properties of its own. A primer or size is generally 0.1 to 10 mm thick and must have adequate mechanical film properties, such as rigidity, tensile strength, and toughness to carry the mechanical load when the composite is stressed. An adhesive is a gap-filling polymer used to bond solid adherents such as metals, ceramics, or wood, whose solid surfaces cannot conform to one another on contact. Pure silanes are rarely used as adhesives; rather, they are used to modify gap-filling polymers or polymer precursors to improve surface adhesion. Silane monomers may be used in integral blends of fillers and liquid resins in the preparation of composites.

Silane chemical structure:

Silane coupling agents belong to the family of organosilicon monomers, which are characterized by the general formula R-SiX$_3$. R represents an organofunctional group attached to the silicon in a hydrolytically stable condition. X is hydrolysable alkoxy groups (usually methoxy, -OCH$_3$ or ethoxy, -OC$_2$H$_5$), which are hydrolyzed into silanol groups. R is usually composed of a reactive group R` separated by a propylene group from silicon, R`-CH$_2$-CH$_2$-CH$_2$-SiX$_3$. The reactive group can be vinyl (-CH=CH$_2$), amino (-NH$_2$), mercapto (-SH) or can contain several chemical functional groups. The attached reactive organic functional group, R`, is specially formulated for the intended resin. Non-organofunctional silanes or silane cross linkers have the general structure 3X-Si-R-Si-X3 where R=(CH$_2$).

Hydrolysis and condensation of alkoxysilanes:

Most silanes are deposited from aqueous solutions or organic solutions containing water. They can also be dry blended with the substrate. But the quality of uniformity is not as good as aqueous solutions. If the silane should interact with an inorganic surface and form chemical bond at the interface, it must be first converted to the reactive silanol form by hydrolysis reaction.

$$R\text{-}SiX_3 + 3H_2O \longrightarrow R\text{-}Si(OH)_3 + 3HX$$

The hydrolysis can occur directly on the substrate surface by reaction with water on the surface or in the resin, or in a previous step during preparation of the aqueous solution of the coupling agent. Adsorption of silane species through siloxane bond on the inorganic materials requires physisorbed water on the surface of substrate[13]. The silanol form of the silane reacts to form dimers or trimers or tetramers according to the reaction

$$\begin{array}{c} OH \\ | \\ R\text{-}Si\text{-}OH \\ | \\ OH \end{array} + \begin{array}{c} OH \\ | \\ HO\text{-}Si\text{-}R \\ | \\ OH \end{array} \longrightarrow \begin{array}{c} OH \quad OH \\ | \quad | \\ R\text{-}Si\text{-}O\text{-}Si\text{-}OH \\ | \quad | \\ OH \quad OH \end{array} + H_2O$$
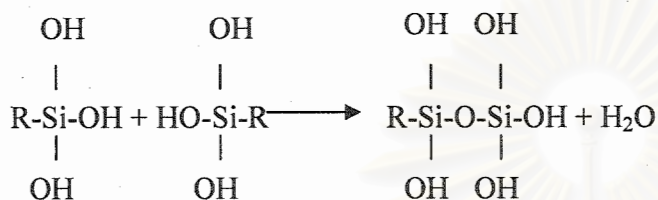
and in time to polymers or it could be grafted onto a hydroxylated surface according to

$$\begin{array}{c} OH \\ | \\ R\text{-}Si\text{-}OH \\ | \\ OH \end{array} + HO - \boxed{\ } \longrightarrow \begin{array}{c} OH \\ | \\ R\text{-}Si\text{-}O \\ | \\ OH \end{array} - \boxed{\ } + H_2O$$
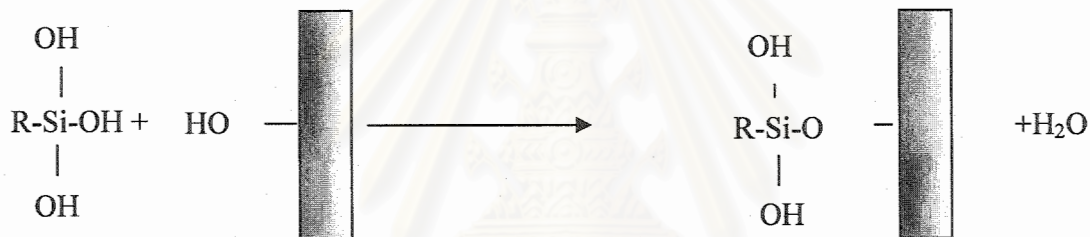
It is important to understand the hydrolysis and condensation reactions which occur simultaneously but the hydrolysis reaction is more rapid for most silanes and the condensation reaction is slower in the presence of slightly acidified water (pH 3-6)[14] Thus, acidic solutions are preferred to maximize silanol species solution. Due to the competitive condensation, the silane concentration should not exceed 1 to 10%, depending on the type of silane.

Most commercial silanes have limited water solubility until the alkoxysilane groups of the silane are converted to hydrophilic silanol groups. To enable the hydrolysis of non water-soluble silanes and to avoid oligomerization, the silanes first have to be

dissolved in an appropriate solvent. Usually an alcohol is used for this purpose. The use of alcohol to promote dissolution of the silane can lead to the backward reaction so called alcoholysis, which can slow down the hydrolysis reaction. An example of this type of reaction is

$$
\begin{array}{ccc}
OC_2H_5 & & OC_2H_5 \\
| & & | \\
R\text{-}Si\text{-}OC_2H_5 + CH_3OH \longrightarrow & R\text{-}Si\text{-}OCH_3 + C_2H_5OH \\
| & & | \\
OC_2H_5 & & OC_2H_5
\end{array}
$$
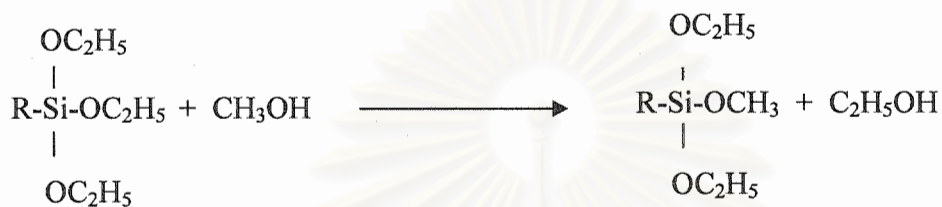
Where the ethoxy group of the silane is exchanged with methoxy group of the alcohol. This will slow down the hydrolysis reaction but will stabilize the silanol solution for a period of time.

Silane coupling agents for reinforced composites are required to fulfill rather complex responses, which may vary with different methods of application. For treatment of fiberglass it is required that the silane be soluble in water, and that dilute aqueous solutions remain predominantly monomeric for at least one day in the treating bath. When dried on the glass surface, the coupling gent must condense to polysiloxane structures that retain a degree of solubility in order to compatible with the matrix resin. During the curing of the composite, it is advantageous if the interphase region, controlling by the coupling agent, is hydrophobic and highly cross-linked.

How to use:

There are two basic approaches for using silane coupling agents. The silane can either be used to treat the surface of the inorganic materials before mixing with the organic resin or it can be added directly to the organic resin.

There are two general methods for treating the surfaces of inorganic filler materials before they are added to the organic resins. Wet method: by mixing slurry of the inorganic materials in a dilute solution of the silane coupling agent, a highly uniform and precise treatment of the inorganic material can be obtained. Dry method: a high shear, high speed mixer is used to disperse the silane coupling agent into the inorganic materials. The silane is generally applied either neat or as a concentrated solution. When compared to the wet method, the dry method is most often preferred for a large-scale production, treating a large amount of filler in a relatively short time and generating relatively little mixed waste. However, it is more difficult to obtain uniform treatment with the dry method.

In dental composite, γ- methacryloxypropyltrimethoxysilane (γ-MPTS), is a popular silane coupling agent used. Mohsen and Craig[15] compared 3-methacryloxy-propyltrimethoxysilane and 3-acryloxypropyltrimethoxysilane in silanation of zirconia-silica through diametral tensile and transverse strength of composite made from two fillers and a urethane dimethacrylate in boiling water. They concluded that γ-MPTS gave the best overall result. In another study by Mohsen and Craig[16], they studied the effect of silanation of fillers on their dispersability by monomer system. In this study, they tested sixteen silane coupling agents and three methods of silanation. The silanes were selected to have a variety of organofunctional and hydrolysable groups. Silanation was performed

from an ethanol-water solution of the silanes and by adding the silanes directly to the filler at room temperature and at the boiling temperature of the silanes. The amount of silane used was that required to produce minimum uniform coverage. They found that the effectiveness of silanation on the dispersion of the filler particles was greater when silanation from ethanol solution, three times the minimum uniform coverage was used, silane contained methoxy rather than ethoxy, trialkoxl rather than dialkoxy compounds, when length and bulkiness of the organic functional group were small and when the organic functional group was methacrylate rather than acrylic. The strength of composites prepared from one of the monomer systems and quartz silanated with methacryloxypropyltrimethoxysilane was higher than those silanated with acryloxypropyltrimethoxysilane.

In an attempt to improve the hydrolytic stability of MPTS, Craig and Dootz[17] studied the effect of mixed silanes on the hydrolytic stability of composites. They silanated the filler for urethanedimethacrylate composite with the mixture of fluoroalkyl-, aminoalkyl-, phenyl-, vinyl-, bis silyl ethane- and 3 methacryloxypropyltrimethoxysilane in an attempt to increase the hydrophobicity of the coupling agent layer by water immersion. Diametral tensile strength was used to evaluate the hydrolytic stability of silane coupling agent. They found that vinyltriethoxysilane increased the hydrolytic stability of the composite.

Nihei et al.[18] studied the hydrolytic stability enhancement of dental composited by using fluoroalkyltrimethoxysialnes. They used trifluoropropyl-, nonafluoroalkyl-, tridecafluorooctyl-, heptadecafluorodecyl and henicosafluorododecyl-trimethoxysilane mixed with 3-methacryloxypropyltrimethoxysilane in different ratios. Tensile strength in

dumbbell-shaped specimens was used to test after immersion of specimens in water for 1,800 days. They concluded that composites which fillers were silanated with fluoroalkytrimethoxysilane were significant higher in tensile strength than those of without fluoroalkyltrimethoxysilane.

Adsorption behavior of a silane coupling agent:

The silane coupling agent forms a multi-layer on the surface of substrate surface. Adsorption of silane coupling agent onto the substrate surface can be classified into two layers. The first layer, covalent bond with hydroxyl group of silica filler, is called chemisorbed silane. This covalent bond is siloxane bond. Once chemisorbed silane is saturated, the second layer starts to deposit onto the first layer through van de Waals or weak hydrogen bond. This layer is called physisorbed. This physisorbed layer can condense together with the same silane coupling agent and become dimer, trimer, tetramer and so on depend upon the condition. Later, Yang et al. also confirmed the two layers of adsorption by using pyrolysis gas chromatography[19].

Adsorption behavior of a silane coupling agent on silica was extensively studied by Nishiyama group. Nishiyama et al[20] studied the effect of drying time and silane concentration using gel permeation chromatography (GPC). They looked into the bonding of the silane to the silica surface, the amount of adsorbed and the molecular species by measuring the extractable, physisorbed silane: γ-MPTS was used in their study. Silanation were performed with γ-MPTS in 70/30 mixture solution of ethanol and water. The concentrations of γ-MPTS studied were 2.7, 5.5, 10.9, 14.0, 22.0, 33.0, and 43.5 mg/ml. Ten grams of colloidal silica with surface area $130m^2/g$ were added to 150 ml of silane solution. Deionized water of pH 5.5 was used to adjust with HCl resulted in 10^{-4}, 10^{-2}, 10^{-1} mole/liter. The concentration of γ-MPTS used was 14.0 mg/ml. They found that chemisorption occured rapidly within 1 day and continued to gradually increase until 14 days. Fourier transform-infrared diffuse reflectance spectroscopy

(DRIFT) was used to obtain information concerning the adsorption behavior of the chemisorbed silane. The effect of acid on the adsorbtion behavior was investigated as a function of acid concentration. They also found that additional of hydrochloric acid increased the molecular weight of the adsorbed silane species. The molecular species chemisorbed on the silica surface was different with different concentration of hydrochloric acid.

Nishiyama et al[21] studied the influence behavior of a silane coupling agent onto silica on visco-elastic properties. They found out that physisorbed silane caused dramatic differences in visco-elastic properties, due to reinforcement. They showed existence of physisorbed layer increased the modulus of elasticity. They also suggested that extra silane coupling agent; physisorbed, stayed at the vicinity of filler not dispersed through the resin matrix.

Soderholm and Shang[22] investigated the molecular orientation of silane at the surface of colloidal silica by diffuse reflectance infrared Fourier transform spectroscopy. The silane studied in this study was γ-MPTS at different concentration and colloidal silica was Cab-O-Sil. They found that critical concentration needed for complete surface reaction and minimum physical γ-MPTS adsorption should be between 0.0325 and 0.065 γ-MPTS /g Cab-O-Sil. These two values suggested that half of the amount calculated for a reaction between one isolated OH-group per MPTS molecule. At the critical concentration, the γ-MPTS molecules were oriented parallel to the Cab-O-Sil surface. Their finding suggested that the silane density on Cab-O-Sil is 1 molecule per 1.04 nm^2 compared to the simulation computation on MPTS molecule which suggested 1 γ-MPTS molecule covered a maximal area of 0.55 nm^2. Consequently, the chemically bonded

silane monolayer, chemisorbed, did not form a complete coverage of the filler surface. They also suggested that the amount of silane coupling agent needed to coverage filler depended upon the number of isolated OH-group on filler surface.

Nishiyama et al[23] studied influence of adsorption characteristics of silane on the hydrolytic stability of silane at the silica-matrix interface. They prevailed what parameter control the hydrolytic stability of the silane multilayer at the silica-matrix interface and the effects of addition of hydrochloric acid to silane solution using gel permeation chromatography and cross-polarization/magic-angle spinning silicon 29 nuclear magnetic resonance (CP/MAS Si[29]NMR). They correlated the adsorption behavior with the hydrolytic stability of the interphase by means of a tensile test. They found that under acidic conditions, the molecular weight of the deposited silane is higher than that deposited in non-acidic conditions. This is due to intermolecular condensation of the silanol group of the silane molecule under acidic conditions. This is mainly attributed to the fact that the acid accelerates the hydrolysis of the methoxy group in the silane molecule. They concluded that hydrolytic stability was based on the available silanol group (Si-OH) available on chemisorbed layer to establish hydrogen bond with physisorbed layer. The additional of acid decreased the hydrolytic stability was due to the species of chemisorbed with lack of available silanol group to have hydrogen bond with physisorbed silane. The hydrolytic stability of the silane was dependent upon the cohesive force of the silane multilayer, especially that between the chemisorbed layer and physisorbed layer. The increased hydrolytic stability is provided by the species which have an increase potential for hydrogen bonding.

Nishiyama et al[24] also studied the effect of heat-treatment on the adsorption behavior of silane couping agent. They studied the effect of heat-treatment applied to the silanated filler on the absorption behavior and hydrolytic stability. They found that heating over 80°C caused chemisorbed multilayer and no silanol group available for hydrogen bond with physisorbed layer. While heat-treatment less than 80°C, there were silanol group available for hydrogen bond with physisorbed. They suggested that chemisorbed monolayer and physisorbed layer were apparently an ideal situation for hydrolytic stability of the silane coupling agent.

Liu et al[25] studied filler-coupling agent-matrix interactions in silica/poly-methylmethacrylate composites. They found that with the aid of vacuum in drying filler at 25°C resulted in two types of adsorbed silane, firmly adsorbed and loosely adsorbed silane. The loosely adsorbed silane could desorb from the silica and be incorporated into the polymer matrix through copolymerization with monomeric methyl methacrylate, resulting in crosslinking of the matrix. When the silanated silica was dried at 110°C for 2 hours, the loosely adsorbed silane was removed and the amount of firmly adsorbed silane increased. This studied was in agreement with Nishiyama[23] study on the heat-treatment of silica that temperature in drying silanated silica over 80°C would force the physisorbed to condense with the previous chemisorbed, resulted in chemisorbed multilayer and no longer had silanol group available.

In conclusion of the adsorption behavior of silane coupling agent, it was clearly demonstrated that silane coupling agent species, molecular weight and condensation among silane molecules reflected the hydrolytic durability of the fillers and silane coupling agent interface. Water at the filler surface plays the important role in

establishing the chemisorption between silane species and the filler surface. The aforementioned literatures supported that chemisorbed monolayer covered filler was essential in providing hydrolytic stability of such interface.

Degradation of composite resin:

The degradation of composite resin in oral environment was believed to occur from resin matrix itself, mismatch between filler and matrix resin in coefficient of thermal expansion and hydrolytic instability of silane coupling agent at the polymer-filler interface layer.

Silane coupling agent has been proven to improve the mechanical properties of composites by facilitating adhesion of inorganic filler particles to polymer matrix. The hydrolytic stability of the composite is also improved by using silanes because of the hydrophobic nature of silane coupling agents. The amount of silane coupling agent used in silanation of the filler is important to protect the silica from the water. Silane coupling agent adsorbed to the silica and in composite resin can be classified as chemisorbed and physisorbed. Chemisorbed silane coupling agent is the silane coupling agent molecules, which has a siloxane bond with the silica surface, while physisorbed is a loose bound between adjacent silane coupling agents with hydrogen bond. The existence of the physisorbed is hypothesized in responsibility to the modulus of elasticity of the composite.

Several studied has performed in order to find the proper method in silanation; surface decontamination[26] and suitable amount of silane coupling agent. Most studies utilized the weight percentage of the filler to calculate the amount of silane used. The common weight percentage are 10[27, 28, 29] and 4[30]. To date, there is no consensus on the amount of silane coupling agent in providing optimum mechanical properties and durability of composite resin in moist environment such as in oral environment.

From the available studies, there is no single study perform to elucidate the effect of silanation method; optimum amount of silane coupling agent, heat treatment and acidity of silanation solution to the whole macroscopic mechanical properties of the composite.

Strength: Flexural strength and flexural modulus:[31]

The transverse strength of a material is obtained when one loads a simple beam, supported at each end, with a load applied in the middle. Such test is called a three-point bending test and transverse strength is often described in technical, dental and engineering literature as the modulus of rupture or flexural strength. When apply load to the top of the beam, the top part is under compression while the bottom part is subjected to tension.

Flexural strength reflected the ability of the material to withstand the stress. The flexural strength, FS, in megapascals was calculated from the following equation:

$$FS = 3Fl/2bh^2$$

where, F is the maximum load, in newtons, exerted on the specimen;

l is the distance, in millimeters, between the supports;

b is the width, in millimeters, of the specimen measured immediately prior to testing;

h is the height , in millimeters, of the specimen measured immediately prior to testing.

Flexural modulus is the property of the material related to the attraction forces within the material. It represents the relative stiffness of the material within the elastic range. This property reflects the strength of the material in resisting the deformation under loading. The elastic qualities of the material represent a fundamental property of the material. The interatomic or intermolecular forces of the material are responsible for the property of elasticity. The stronger the basic attraction forces, the greater the value of the elastic modulus and the more rigid or stiff material is. Because this property is related to the attraction forces within the material, it is usually the same when material is

subjected to either tension or compression. The property is generally independent of any heat treatment or mechanical treatment that the material has received, but it is quite dependent on the composition of the material. The elastic modulus is determined by the slope of the elastic portion of the stress-strain curve, which is calculated by choosing any two stress and strain coordinates in the elastic or linear range.

Flexural modulus, E, in megapascals was calculated from the following equation:

$$E = Fb/4bh^3d$$

where, F is the load, in newtons, at a convenient point in the straight-line portion of the trace;

d is the deflection, in millimeters, at load F;

l,b and h are as the same as flexural strength.

CHAPTER II

OBJECTIVES AND HYPOTHESES

The interface between two dissimilar materials, filler and resin matrix, plays an important role in reinforcement of composite. Silane coupling agent has been introduced with the effort to join two dissimilar materials as one whole material so-called composite. In dentistry, resin composite has been widely used and accepted functionally and esthetically. Intraoral environment subjects the material under stress and moist harsh environment. Therefore, the composite placed in the cavity of the teeth as a restorative material and/or as a foundation of the tooth replacing loss of structure should be strong to withstand the repeated stress and must possess a stable hydrolytic stability. It is always a quest in the dentistry to come up with material, which has the properties as close as natural enamel and dentin or better. Previous studies had been performed to find a better monomer and filler. Acceptable monomer and filler are currently used in manufacturing composite. But the know how on using silane coupling agent has not been clearly and extensively performed to elucidate the proper processing. Currently, manufactures make composite by using silanated filler which was silanated following empirical approaches as their own experience. Therefore, this study has been carried out in an attempt to establish a scientific approach to clarify the potential effects of the silanation processes; amount of silane coupling agent, heating treatment and pH of silanating solution on flexural properties and hydrolytic durability of composite.

Objectives:

The objectives of the study are as follows:

1.   To find the better resin matrix used in the study by comparing between UDMA/TEGDMA and BisGMA/TEGDMA monomer system in terms of flexural properties.

2.   To find the optimum amount of silane coupling agent required in covering the silica fillers that provides better strength and hydrolytic durability to the experimental composite resin.

3.   To evaluate the heat-treatment effect of fillers prior to mixing with resin matrix and the addition of hydrochloric acid in silanating soloution to the strength and hydrolytic durability of experimental composite resins.

Hypotheses:

The hypotheses are as follows:

1.   UDMA/TEGDMA and BisGMA/TEGDMA possess the same flexural properties and hydrolytic durability of resin matrix.

2.   The different amount of silane coupling agent covering filler has no effect on flexural properties and hydrolytic durability of composite.

3.   The difference in heat treatment in drying filler after silanation has no effect on flexural properties and hydrolytic durability of composite.

4.   The difference in acidity of silanating solution has no effect on flexural properties and hydrolytic durability of composite.

CHAPTER III

DETERMINATION OF RESIN MATRIX IN TERMS OF

HYDROLYTIC DURABILITY

INTRODUCTION

Most of resin matrices used in dental resin composite are mainly BisGMA and UDMA as a main monomer and TEGDMA as the diluent for adjusting working viscosity. Asmussen and Peutzfeldt[32] compared the influence of monomer ratio on mechanical properties of the experimental resin composites. They varied several mixing ratios and tested on diametral tensile strength, flexural strength and elastic of modulus. It was concluded that by varying mixing ratio could come up with specific mechanical properties. Indrani et al[33] evaluate the fracture toughness of experimental composite using several combinations of monomer frequently used in the resin composite formula. It was demonstrated that UDMA/TEGDMA combination provided higher fracture toughness than BisGMA/TEGDMA. They also found that water adsorption of BisGMA/TEGDMA was higher than UDMA/TEGDMA. Nevertheless, there is no study evaluated the two combination of two monomers based on UDMA and BisGMA with TEGDMA as the diluent on hydrolytic durability.

Therefore, the objective of this study was to compare the flexural properties and hydrolytic durability of the two resin matrices. It was hypothesized that there was no differences between two resin matrices in terms of flexural properties and hydrolytic durability.

MATERIALS & METHODS

Two resin matrices, one was a combination of BisGMA and TEGDMA and another was a combination of UDMA and TEGDMA, were evaluated for hydrolytic durability by means of flexural properties.

The resin matrix of all experimental composite was 70/30 mass% of urethane dimethacrylate (UDMA; Art resin SH-500B, Negami Chemical, Ishikawa, Japan) and triethyleneglycol dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan) or BisGMA (Polyscience, USA) and triethyleneglycol dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan). Zero point five mass% of camphorquinone (Aldrich Chemical, Milwaukee, Wis) and 1.0 mass% of dimethylaminoethylmethacrylate (DMEAMA; Wako Pure Chemical, Osaka, Japan) were used as the photoinitiator and reducing agent, respectively. All materials were used as received without any further purification. The 2x2x25 mm rectangular specimen was fabricated as suggested in ISO 4049:2000 (Fig 3.1).[31]
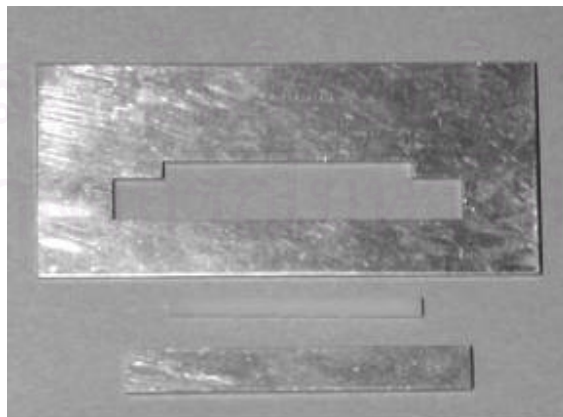
Fig 3.1 Mold and specimen according to ISO 4049

Forty-eight specimens, 24 from each composite, were fabricated from two experimental neat resins. The specimen was irradiated using a laboratory light-polymerizing unit (Labolight II, GC, Tokyo, Japan) for 3 minutes from each side of specimen. The specimen was later kept in the 37°C water. After 24 hours storage in the incubator at 37°C, six specimens were randomly selected from each group and tested for baseline value at day 0. The remaining specimens were then placed in the Soxhlet's extractor (Sibata, Tokyo, Japan) and subjected to boiling water condition for additional 1, 7 and 28 days (Fig 3.2). At the end of each time, six specimens were again randomly selected and tested. All specimens were subjected to a 3-point bending test in 37°C water using micro material test machine (MMT-250N, Shimadzu, Kyoto, Japan) (Fig 3.3). Flexural strength (FS) and flexural modulus (FM) were obtained from each test using analyzing software (Trapezium II, Shimadzu, Kyoto, Japan). The FM was calculated from the slope of the stress- strain curve between 5-20 N/mm^2.
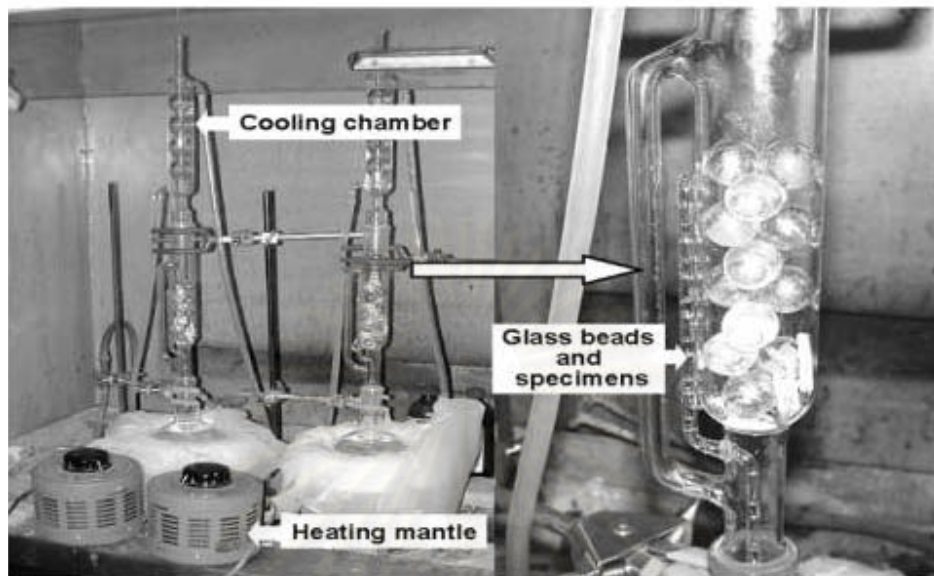
Fig 3.2 Soxhlet's extractor
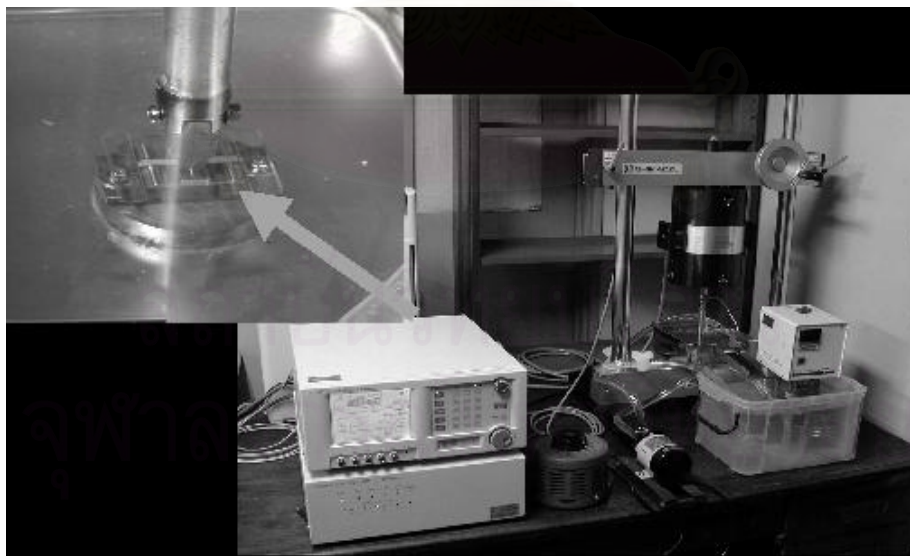
Fig 3.3 MMT-250N and experiment set up

RESULT

The FS and FM values are summarized in Table 3.1. The FS and FM of the UDMA/TEGDMA mixture were greater than those of the BisGMA/TEGDMA at all time. UDMA/TEGDMA showed better hydrolytic durability while BisGMA/TEGDMA degraded over time. At 7 and 28 days after immersion in Soxhlet's extractor, the BisGMA/TEGDMA showed very low in FS that was too low for calculation of FM. Specimens after one-day storage in Soxhlet's extractor demonstrated crazing (Fig 3.4). Since the data were so obviously different, statistic analysis was not performed. Two-way ANOVA revealed significant differences only in the main factor; type of monomer, at $p < 0.0001$ of FS. Since the FM of BisGMA/TEGDMA could not be calculated due to crazing and undetectable FM from stress and strain curve, comparison between FM of original values was performed using student t test. Statistic analysis revealed significant difference between UDMA/TEGDMA and BisGMA/TEGDMA at $p < 0.0001$.

Table 3.1   FS and FM of BisGMA/TEGDMA and UDMA/TEGDMA

Days	BisGMA/TEGDMA (n=6) Flexural strength (MPa±sd)	UDMA/TEGDMA (n=6) Flexural strength (MPa±sd)
0	26.3±2.8	49.4±1.8
1	11.9±2.3	51.2±5.7
7	6.5±0.8	53.8±6.8
28	6.0±0.5	60.1±3.9

Days	BisGMA/TEGDMA (n=6) Flexural modulus (GPa±sd)	UDMA/TEGDMA (n=6) Flexural modulus (GPa±sd)
0	0.39±0.04	1.05±0.09
1	0.52±0.01	0.96±0.12
7	N/A	1.08±0.07
28	N/A	1.21±1.16

Fig 3.4 showed crazing of BisGMA/TEGDMA specimens on the left and UDMA/TEGDMA specimens on the right

DISCUSSION

The dimethacrylates BisGMA and 1,6-bis(methacryloxy-2-ethocycarbonylamino) -2,4,4-trimethylhexane (UDMA) are widely used as the primary or base monomers in the formation of the polymeric matrices of dental composites. These two monomers are comparable in size but differ in their chemical structure features which affect critical properties such as viscosity, diffusivity, polymerization, vinyl conversion, shrinkage, water uptake, optical match with reinforcing fillers, physicochemical and mechanical properties. A common feature of BisGMA and UDMA is their ability to form physical crosslinks via hydrogen bonding that can augment the basic strength and modulus of their dimethacrylate-based polymers that is principally achieved by carbon-carbon covalent bonding, especially in the form of chemical crosslinks of the network structure.

This study was designed to ascertain the find out the better comonomers in regards of better hydrolytic durability and better mechanical properties. The better comonomer will be used in the following experiments.

The use of Soxhlet's extractor has been shown to be effective in degrading the resin matrix. Soxhlet's extractor was heated with a heating mantle and the evaporated water was condensed in a cooling chamber, therefore, distilled water was always circulated within the Soxhlet's extractor. To prevent rapid temperature reduction, glass beads, diameter 16.5mm (Seiwa-riken, Tokyo, Japan) were placed inside the extractor as shown in Figure 2. The Soxhlet's extractor is generally used for extracting substance

from solid compound. This apparatus was used in order to generate moist heat stress to resin matrix with anticipation of hydrolysis of the components.

The result showed that UDMA/TEGDMA combination of resin matrix was more hydrolytic stable and possessed better mechanical properties. This is in agreement with previous studies.[31,34] This might be due to the higher conversion ratio obtained from each monomer. Since UDMA chemical structure is more flexible resulted from lack of benzene rings in the chain, therefore motility of monomer is better and creates more chance for polymerization with the neighbour molecule resulting in higher conversion ratio. The chemical structure of BisGMA contains two hydroxy groups per molecule. These hydroxy groups can form the hydrogen bond between molecules. The resultant of the hydrogen bond makes the BisGMA high viscosity in nature and is prone to hydrolytic degradation at these sites demonstrated in more water sorption. The hydrolytic degradation of the polymer may result from scissor of ester linkage in the molecule.[35] In the process of BisGMA synthesis, initial precursors are bisphenol A and diglycidyl dimethacrylate. The resultants of such a chemical reaction were previously reported, however BisGMA used this study was relatively quite pure material. The byproduct such as salt of bisphenol A, glycidyl ether of a bisphenol , glycidyl methacrylate and/or bisphenol A can be impurities These may act as the decontaminants and perhaps may be the oxidizing agents causing reduction in FS and crazing of BisGMA/TEGDMA as shown in Fig 3.4.

CONCLUSION

  From the result obtained and within the limit of this study, it was concluded that Soxhlet's extractor is effective in causing degradation of composite and UDMA/TEGDMA is more hydrolytic stable than BisGMA/TEGDMA. In order to gain an insight investigation on effect of silane coupling agent, the more hydrolytic stable copolymer must be selected. Therefore, UDMA/TEGDMA was selected in the further study for evaluation of hydrolytic stability of experiment composite.

CHAPTER IV

EFFECTS OF SILANE COUPLING AGENT AMOUNT ON MECHANICAL PROPERTIES AND HYDROLYTIC DURABILITY OF COMPOSITE RESIN AFTER HOT WATER STORAGE

SYNOPSIS

The purpose of this study was to evaluate effects of the amount of silane coupling agent on the flexural properties and hydrolytic durability on an experimental composite resin for understanding the optimum amount of silanation. A spherical filler was silanated with 7 different amounts of γ-MPTS, 0, 0.17, 0.34, 0.66, 1.36, 2.72 and 5.45 mass%. Photo-polymerized experimental composite resins were made from 70/30 mass% of UDMA/TEGDMA and 65 mass% of different silanated amount of filler. Bar-shaped specimens were prepared for a 3-point bending test at 37ºC water after 1-day water storage at 37ºC and after the additional 1, 7, and 28 days hot water storage in Soxhlet's extractor. The flexural strength and flexural modulus of unsilanated filler dramatically decreased after 28 days hot water storage while those of silanated filler showed a slightly change. These results suggested that the silanated amount on the silica filler is not sensitive for flexural properties and hydrolytic stability of composite resin.

INTRODUCTION

Modern dental composite resins demonstrated improved mechanical properties and were widely used in many applications but the durability of composite resins is still ambiguous. The degradation of composite resin in oral environment is considered to occur from resin matrix[8, 36, 37] the degradation of filler particle[8, 38, 39] and hydrolytic instability of silane coupling agent at the polymer-silica interface layer.[40, 41] With respect to hydrolytic stability of the coupling agent, there are several approaches to improve coupling ability by novel silane coupling agents and/or the suitable silanation processes such as amount of silane coupling agent, heat application during silanation and pH of the silanation vehicle. More hydrolytic durable coupling agents were achieved by newly synthesized polyfunctional silanes.[18, 42, 43] However, the conventional coupling agent, gamma-methacryloxypropyl-trimethoxysilane, γ -MPTS, is still popular in silanating fillers.

The silane coupling agent adsorbing on the fillers creates bi-layer, chemisorbed and physisorbed silane layers. The chemisorbed silane is adsorbed on the surface with covalent bond. The physisorbed layer is a loosely bounded layer over the chemisorbed layer by hydrogen bond and van der Waals force among silane coupling molecules. Recently, Wang and Jones[44] confirmed the deposited structure of γ-aminopropyltriethoxysilane (γ-APS) on glass surface. Three layers from the glass surface are advocated: two types of the chemisorbed layer, a high hydrolytic resistance grafted "interfacial" layer and a removable chemisorbed layer, and the outer physisorbed layer. The physical and mechanical properties of this network depend on the nature of the silane deposited on the filler; i.e. amount of

coupling agent, pH, rate of hydrolysis and condensation, and the drying condition used in silanation.

The amount of the silane coupling agent on the filler is important because the silane coupling agent creates a suitable filler morphology or thickness of silane for protecting filler from the hydrolytic degradation. Such an interface/ interphase region plays some roles in determining mechanical properties and provides durability of the composite materials. Therefore, this study will focus on the amount of silane coupling agent absorbed on silica surface. To date, there is no consensus on the amount of silane coupling agent, covering silica in providing optimal mechanical properties and durability of composite resin in moist environment such as in oral environment. Most studies utilized the mass percentage of the filler to calculate the amount of silane coupling agent used. The common empirical amount were 10 mass%[27-29] and 4 mass%[30]. Mohson and Craig[16] advocated three times of the recommended coverage amount based on surface area of silica and surface coverage of silane coupling agent suggested by Akles.[45] The existence of the excess amount over uniform coverage is hypothesized in responsibility to the modulus of elasticity and to provide a more hydrolytic durability to the composite.

Therefore, the purpose of the present study was to find the optimum amount of silane coupling agent based on the surface area and number of functional group of silane coupling agent that required in covering the silica filler, which provided both better mechanical properties and the durability.

MATERIALS AND METHODS

Silanation of filler

The filler used in the present study was spherical-shaped silica filler (SS15, Osaka Chemical, Osaka, Japan), 1.5 mm in diameter, surface area of 2.06 m^2/g, and density of 2.2 g/cm^3. Gamma-MPTS (KBM 503, Shin-Etsu Chemical, Tokyo, Japan) was used in silanating the filler. Seven concentrations in mass percentage of γ-MPTS, calculated based on surface area of filler and coverage surface area of γ -MPTS, used in silanation were 0, 0.17, 0.34, 0.66, 1.36, 2.72, and 5.45 mass%. The amount of coupling agent used in this study was based on the wetting surface area of silane and surface area of filler. The relationship of amount of coupling agent to obtain a minimum uniform coverage is the equation suggested by Arkles.[45] The surface area of the filler used the present study was 2.06 m^2/g and γ -MPTS can cover the silica on 314 m^2/g. Therefore, one gram of the filler theoretically requires 0.0066 g of γ -MPTS (0.66%) for monolayer coverage. This proposed amount was 7.7 molecules/ $1nm^2$ of the filler surface area. Then, the amounts of the silane coupling agent, 0.17, 0.34, 0.66, 1.36, 2.72 and 5.45 mass% were 2, 4, 7.7, 16, 32, 64 molecules/ $1nm^2$, respectively.

The filler was silanated using 70 mass% ethanol aqueous solution at room temperature. After silanation, the filler was left dry at 25°C for 14 days prior to mix with resin matrix.

Characteristics of silanated filler

Silanated filler of each concentration was investigated to identify absorbed molecular on the filler using a Fourier transform infrared spectroscopy, (FTIR-8300, Shimadzu, Kyoto, Japan) equipped with a diffuse reflectance apparatus. Spectra were obtained from the co addition of 200 scans at a resolution of 4 cm^{-1}on a mixture of filler and KBr.

Silanated filler of each concentration was examined to understand its characteristics by an organic element analysis. Silanated fillers before and after organic solvent cleaning were examined to confirm amounts of adherent silane coupling agents on the filler surface using an organic element analyzer (CHS recorder MT3, Yanaco, Tokyo, Japan). Silanated filler from each group was dispersed in tetrahydrofurane, THF, (Wako Pure Chemical, Osaka, Japan) and stirred. After stirring, the suspension was centrifuged discarded and the silica residue was rinsed with THF again. This procedure was repeated until the UV peak at 225 nm due to γ -MPTS was not observed in the supernatant solution. The filler was then dried at room temperature. Percentage amounts of ash, carbon of fillers were analyzed. Four to 10 mg of fillers were heated at 950ºC for burning, 850ºC for oxidization and 550ºC for reducing with air and oxygen purging at 200 and 20 ml/min, respectively. The measurements were performed twice. The amounts of γ -MPTS were computed from the detected carbon weight based on the mass composition of carbon in γ -MPTS molecule. This carbon ratio was assumed to be 40.7 mass%. The molecular ratio of γ -MPTS on the filler was calculated using specific surface area of the filler, 2.06 m^2/g.

Composite resin specimens for mechanical evaluation

The resin matrix of all experimental composite was 70/30 mass% of urethane dimethacrylate (UDMA; Art resin SH-500B, Negami Chemical, Ishikawa, Japan) and triethyleneglycol dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan). Zero point five mass% of camphorquinone (Aldrich Chemical, Milwaukee, Wis) and 1.0 mass% of dimethylaminoethylmethacrylate (DMAEMA; Wako Pure Chemical, Osaka, Japan) were used as the photoinitiator and reducing agent, respectively. All materials were used as received without any further purification. The 2x2x25 mm rectangular specimen was fabricated as suggested in ISO 4049:2000.[31] The filler loading in all experimental composite resins was kept constant at 65 mass%. One hundred and sixty-eight specimens, 24 from each composite, were fabricated from seven experimental composite resins. The specimen was irradiated using a laboratory light-polymerizing unit (Labolight II, GC, Tokyo, Japan) for 3 minutes from each side of specimen. The specimen was later kept in the 37°C water. After 24 hours storage in the incubator at 37°C, six specimens were randomly selected from each group and tested for baseline value at day 0. The remaining specimens were then placed in the Soxhlet's extractor and subjected to boiling water condition for additional 1, 7, and 28 days. At the end of each time, six specimens were again randomly selected and tested. All specimens were subjected to a 3-point bending test in 37°C water using a micro material test machine (MMT-250N, Shimadzu, Kyoto, Japan). Flexural strength and flexural modulus were obtained from each test using analyzing software (Trapezium II, Shimadzu, Kyoto, Japan). The data were analyzed using 2-way ANOVA and Tukey HSD. The statistic significance was considered at $p<0.05$.

SEM observation

Fracture surfaces of specimens after the flexural test were gold sputter coated and examined by secondary electron imaging using a scanning electron microscope (Hitachi S-4500, Tokyo, Japan).

RESULTS

FTIR

Typical spectra of measured fillers are demonstrated in Fig 4.1.
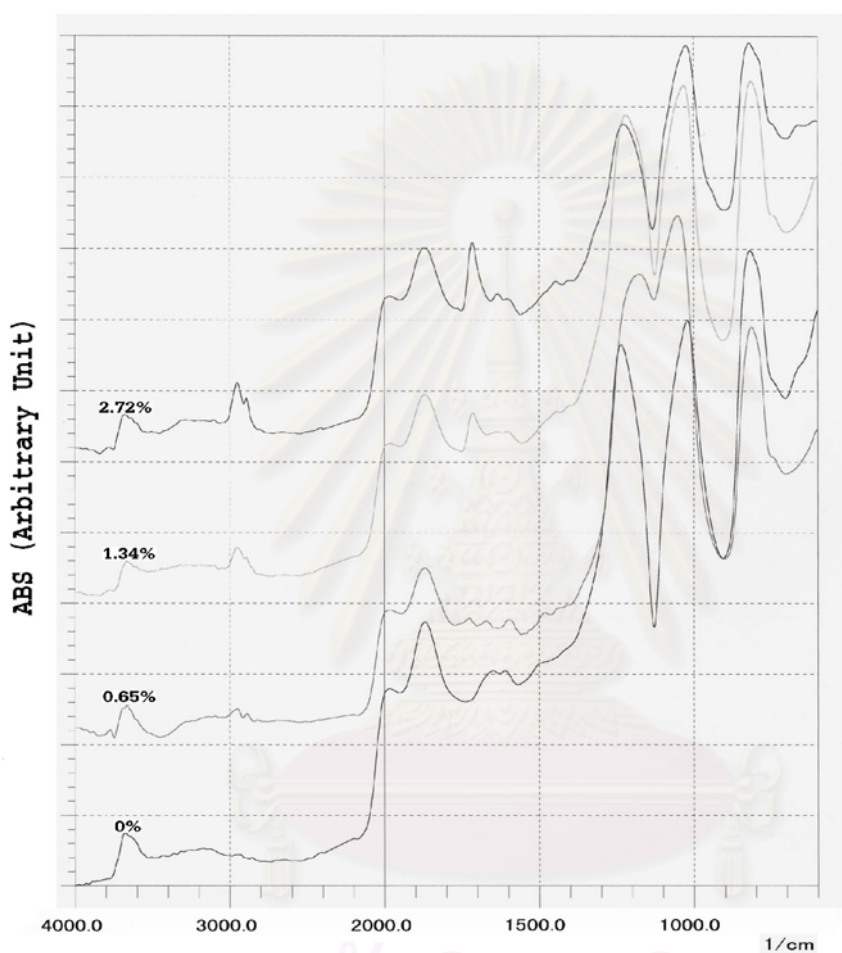
Fig. 4.1 FTIR spectra of different amount of γ-MPTS silanated on filler

All spectra of silanated filler demonstrated the C-H stretching at 2880 cm^{-1} and 2960 cm^{-1}, while C-H stretching did not show on unsilanized filler (Fig 4.1). The presence of the peak around 1700 cm^{-1} in the filler was attributed to the carbonyl group existed in the γ - MPTS molecule.

Organic elemental analysis

Figure 4.2 showed the detected amount of γ -MPTS molecule before and after THF cleaning. Before THF cleaning, the γ -MPTS amount increased with the increasing of silanated amount of γ -MPTS. The organic elemental analysis could not detect the carbon content in 0.17% group due to the small amount of γ -MPTS, which was less than a detectable limit of the apparatus. Therefore exact amounts of silanated coupling agents of all fillers could not be calculated. While the detected amount of γ -MPTS molecule after THF cleaning did not change regardless of increase silanated amount of γ -MPTS. The amount of silane chemisorbed on the silica increased with an increase of the silane amount in the treated solution. When the silane concentration was above 0.66%, the chemisorbed amount of silane was leveled off. This implied that the saturated amount of silane chemisorbed on the 1 nm^2 of silica surface was approximately 8 molecules. The silane molecules, which could not form chemisorption on the silica surfaces, existed on the chemisorbed silane layer as a physisorbed silane.
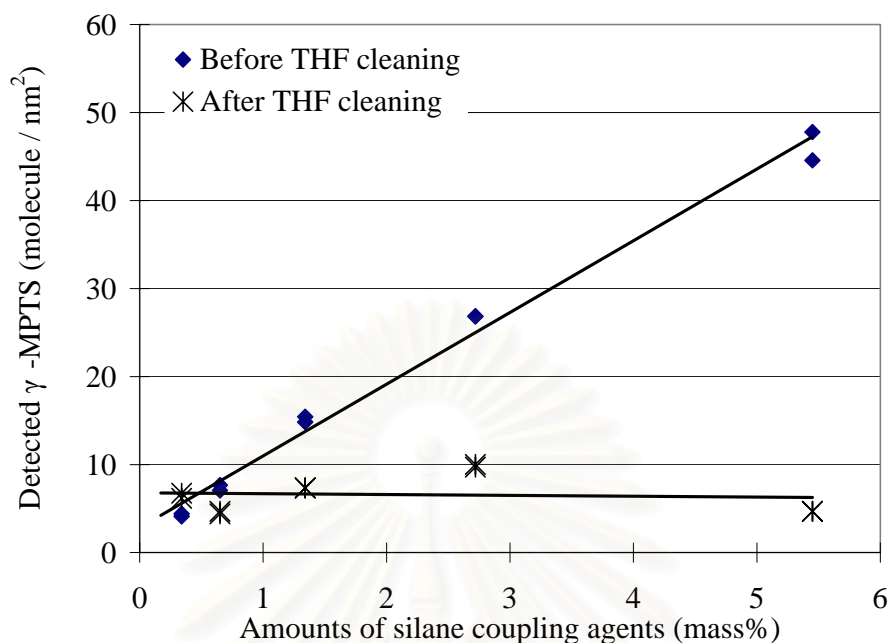
Fig 4.2 Detected amount of γ-MPTS molecule from various silanated amounts before and after THF cleaning

Flexural strength and flexural modulus

The flexural strength (FS), flexural modulus (FM) and their standard deviations are shown in Table 4.1. The flexural strengths of the unsilanated group, 32.4 to 47.8 MPa, were smaller than those of silanated groups, 96.6 to 119.0 MPa. The flexural strengths slightly increased at 1 or 7 days storage. The flexural moduli at 0 day, 3.1 to 3.6 GPa, were almost similar regardless of silane amounts. The flexural moduli of silanated groups slightly increased at 1 or 7 days storage, while those of the unsilanated group decreased with longer storage periods. Because the data between unsilanated and silanated groups were so greatly different therefore unsilanated group was excluded from statistic analysis. For both flexural strength and flexural modulus of silanated groups, 2-way ANOVA revealed significances of two main factors, amounts of silane coupling agent and immersion periods, not their

interaction (Table 4.2 and 4.3). Regarding amounts of silane coupling agent, flexural strengths of 0.66% and 1.36% group were significantly greater than 0.17% group (Fig 4.3). While flexural moduli of 0.34% group was significantly greater than 5.45% group. Regarding effect of immersion period, flexural strengths after 1 and 7 days boiling water storage were significantly greater than that of 0 day boiling water storage (Fig 4.4). The flexural modulus of 0 day was significantly smaller than those of the others.

Table 4.1 Flexural strengths (FS; MPa) and flexural moduli (FM; GPa) after hot water storage

Storage period (day)	Amount of coupling agent (mass%)						
	0	0.17	0.34	0.65	1.36	2.72	5.45
FS							
0	43.8 ± 5.4	96.6 ± 5.2	103.1 ± 8.7	111.3 ± 7.7	112.8 ± 9.4	105.0 ± 6.8	102.2 ± 12.8
1	47.8 ± 4.3	113.4 ± 8.3	113.1 ± 8.2	112.7 ± 10.1	117.4 ± 13.8	117.6 ± 7.3	108.8 ± 11.8
7	41.5 ± 3.8	110.1 ± 10.0	115.4 ± 6.5	115.7 ± 13.8	118.0 ± 19.2	116.9 ± 9.6	109.2 ± 12.2
28	32.4 ± 1.7	99.7 ± 2.6	109.7 ± 6.5	119.0 ± 12.8	110.4 ± 12.0	114.2 ± 17.7	113.7 ± 11.7
FM							
0	3.5 ± 0.6	3.2 ± 0.4	3.6 ± 0.5	3.6 ± 0.3	3.6 ± 0.4	3.4 ± 0.1	3.1 ± 0.3
1	3.1 ± 0.4	3.9 ± 0.4	3.9 ± 0.5	3.7 ± 0.2	3.8 ± 0.6	3.9 ± 0.4	3.2 ± 0.5
7	1.8 ± 0.2	3.8 ± 0.3	4.1 ± 0.3	3.5 ± 0.3	3.9 ± 0.3	3.9 ± 0.3	3.8 ± 0.3
28	1.2 ± 0.1	3.4 ± 0.9	3.7 ± 0.5	3.9 ± 0.3	3.8 ± 0.5	3.7 ± 0.4	3.6 ± 0.3

±: s.d, n = 6

Table 4.2 Result of 2-way ANOVA regarding flexural strength

Factors	DF	Sum of Squares	Mean Square	F Ratio	Probability
A: amount of coupling agent	5	1833	366.6	2.84	0.019
B: immersed period	3	1887	629.0	4.87	0.003
A × B	15	1269	84.6	0.65	0.824
Error	120	15516	129.3		
Total	143	20505			

Table 4.3 Result of 2-way ANOVA regarding flexural moduli

Factors	DF	Sum of Squares	Mean Square	F Ratio	Probability
A: amount of coupling agent	5	23391	4678	2.92	0.016
B: immersed period	3	30778	10259	6.41	0.001
A × B	15	27996	1866	1.17	0.308
Error	120	192174	1601		
Total	143	274339			
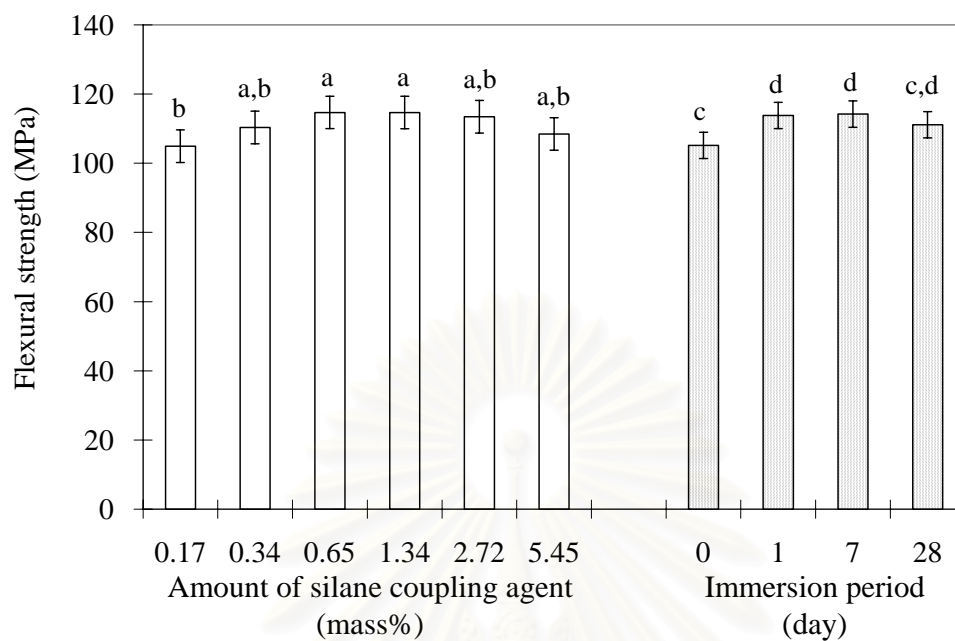
Fig 4.3 Effects of amount of silane coupling agent and immersion period on flexural strength. Bars with the same superscript were not significantly different (p>0.05).
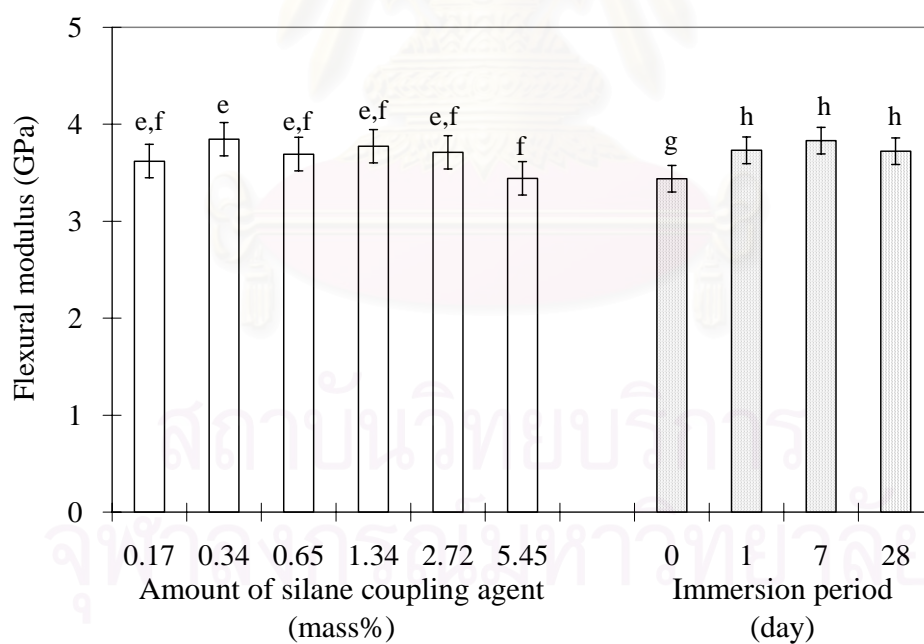
Fig 4.4 Effects of amount of silane coupling agent and immersion period on flexural modulus. Bars with the same superscript were not significantly different (p>0.05).

SEM observation

Figure 4.5 shows a typical different SEM image of the fracture surfaces between unsilanated and silanated groups. The unsilanated group obviously showed filler surface without resin matrix coverage. Therefore, the fracture of the unsilanated group was considered to occur at the interface between the fillers and matrix resin. On the contrary, the silanated group exhibited coverage of matrix resin on the filler surface. This finding suggested good bonding between fillers and matrix resin when fillers were silanated. There were no obvious differences at the fracture surfaces among the silanated groups.
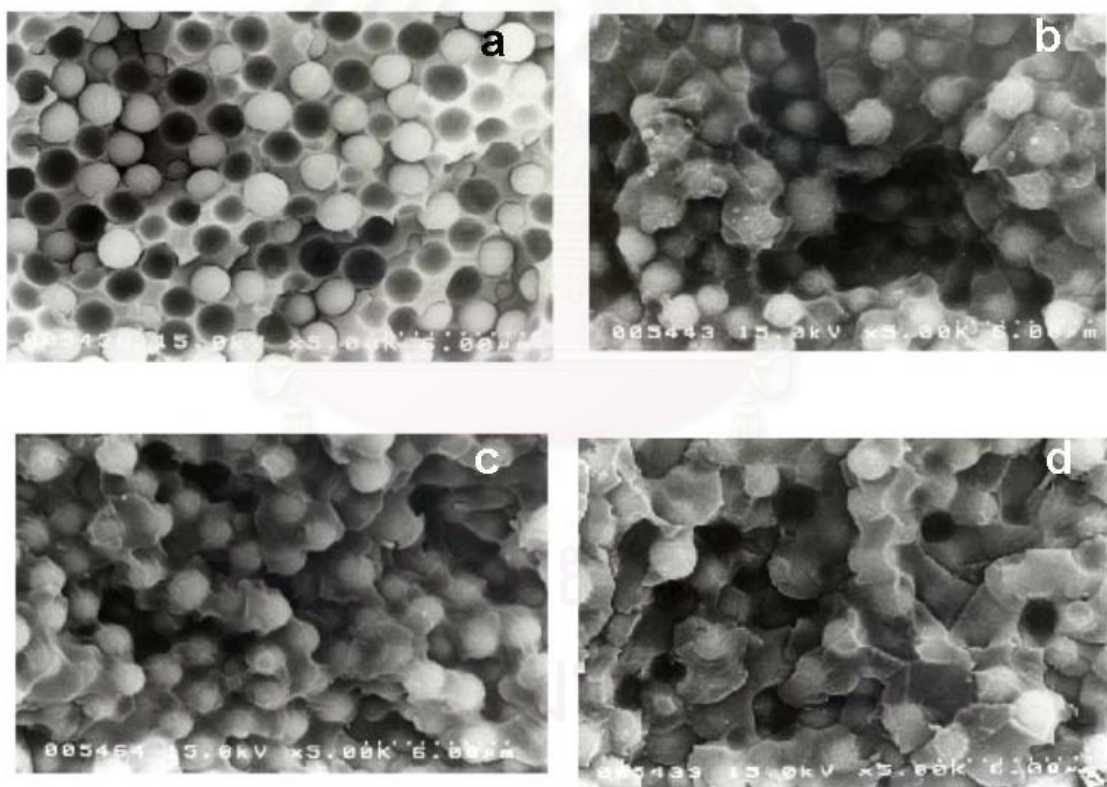
Fig 4.5 Typical SEM images of the fracture surfaces after 28-day hot water immersion. a: unsilanized, b: 0.17 mass%, c: 0.66 mass%, d: 5.45 mass%

DISCUSSION

The spectra obtained from FTIR confirmed the existence and effectiveness of silanation process. The carbonyl stretching was found at 1720 cm^{-1} only in silanized filler. The absorbance peaks at 2880 cm^{-1}, and 2960 cm^{-1} attribute to the C-H stretching in γ-MPTS molecule. The 1880 cm^{-1} absorption peak observed in all spectra is the overtones of the silica network in silica filler[46] The shift toward lower wave number of carbonyl group which indicates the hydrogen bond between the γ -MPTS molecules physisorbed layer could not be detected.[47] The spectra obtained could not confirm the existence of the hydrogen bond between the adjacent γ -MPTS molecules. Hydrogen bonding between carbonyl functionality of γ -MPTS and the substrate moiety is a specific interaction which is unique to molecules at the substrate- absorbate interface which varies among substrates.[47]

The result from the organic elemental analysis suggested at least two types of silane layer adsorbed on silica surface. One layer, chemisorbed layer, could not be removed through rinsing filler by THF. The second layer could be easily removed by THF, physisorbed layer. The amount of chemisorbed silane increased with an increase amount of the silane coupling agent in the silane solution until saturation. The amount over 0.66% then became physisorbed silane as demonstrated in Fig 4.2. This finding was not in agreement with Nishiyama et al[48], which studied on colloidal silica. They found that the saturated chemisorbed amount of γ -MPTS occupied 1 nm^2 of silica surface was 2 molecules. This amount was found as a specific property of γ -MPTS regardless of substrate as demonstrated by Miller and Ishida[47] on clay and lead oxide. The difference in characteristic of absorption may be due to the effect of filler size, which both studies used very small particle size. The

greater amounts of silane than previous reports were attributed to the adsorption of the silane oligomer. The condensation reaction of the silane molecules on the silica surface simultaneously occurs along with the condensation among the silane molecules with a slower rate. Therefore, a higher molecular weight molecules such as tetramer or trimer or dimer, would be chemisorbed on the silica surface. SEM images showed the interfacial fracture only in unsilanated group. The unsilanated group was degraded upon subjecting to moist heat in Soxhlet's extractor. This indicated that the Soxhlet's extractor could accelerate degradation of the composite resins. The accelerated aging using Soxhlet's extractor was intended to promote the hydrolysis of silane layer. But only slightly decreased in flexural strength and flexural modulus of the silanated composite were observed over time. This may be due to the reversible bonding characteristic between physisorbed and chemisorbed layers. The present study showed that the filler silanated with slightly below or over the amount of silane coupling agent calculated by the equation of Arkles was adequate to provide the composite with strength and hydrolytic durability. The effect of the amount of silane coupling agent on filler was similar to the report by Wang and Jones.[49]

The initial flexural modulus decreased as the amount of physisorbed silane increased. If the silane molecule dispersed in the resin matrix, the modulus would decrease due to plasticizer effect of silane molecules.[21] The flexural moduli of silanated groups increased after 1 day boiling water storage. This can be explained by the effect of heating from Soxhlet's extractor caused postpolymerization of matrix resin. The result elucidates that amount of the silane has slightly effect on the flexural strength and the hydrolytic durability of composite resin.

The silane coupling agent forms a bi-layer consisting of the chemisorbed and the

physisorbed silane species on filler surface. The interface is maintained at the equilibrium, which allows for effective stress transfer between the matrix and filler resulting in a composite with high strength, high modulus and hydrolytic durabiliy. Therefore, manufacturers can tailor the composite resin properties by varying the amount of silanation. The effect of the silanated amount is not sensitive in flexural properties and durability as shown in the present study. Specifically, the physisorbed silane species does not affect the hydrolytic stability of the composite resin.

CONCLUSION

The effects of the amount of silane coupling agent on the flexural properties and hydrolytic durability on an experimental composite resin were evaluated to understand the optimum amount of silanation. Within the limit of the present study, even the small amount of silane coupling agent can provide composite with good flexural properties and durability after 28 days of hot water storage.

CHAPTER V

EFFECTS OF HEAT AND pH IN SILANATION PROCESS ON FLEXURAL PROPERTIES AND HYDROLYTIC DURABILITY OF COMPOSITE RESIN AFTER HOT WATER STORAGE

SYNOPSIS

The objectives of this study were to evaluate the effect of heat application after silanation and the pH effect of silanated solution on flexural properties and hydrolytic durability of experimental composites. A spherical-shaped filler was silanated with 0.66 mass% of γ-MPTS in 70% ethanol solution. For heating effect, the filler was heated after silanation for 3 hours at 50, 80 and 110ºC. For the effect of pH, the ethanol solutions with HCl solution of pH 1, 2 and 4 were used. All fillers were mixed to make photopolymerized experimental composite resins. All specimens after immersion in water at 37ºC for 24 hours were additionally immersed in Soxhlet's extractor for another 1, 7 and 28 days. A three-point bending test was performed in 37°C water. The application of heat of 50ºC and 80ºC increased flexural strength while heat of 110°C and pH showed no effects on flexural properties at $p < 0.05$.

INTRODUCTION

The use of composite resin in restorative dentistry has gained popularity due to the esthetics concern and mercury awareness from amalgam restoration. Moreover, the ease of manipulation, conservative preparation, polymerization at operator's desire and the improvement of dentin bonding have made this material more popular. The durability of composite resin placed intraorally should be maintained to ascertain the long-term success of the restoration. From previous studies, the degradation of composite is believed to occur from resin matrix,[8, 36, 37] the degradation of filler[8, 38, 39] and hydrolytic instability of silane coupling agent at the polymer and filler interface.[40, 41]

There were several methods used in evaluation of durability; thermocycling, immersion in water[50, 51] and solvent[41], cyclic loading[50, 52], biological stimulated deterioration utilizing specific enzyme[53] and thermal stress in water and ethanol.[54] Among these various accelerated aging methods, thermal stress by boiling is considerably suitable to evaluate the durability as shown in the previous studies.[16]

Several studies have been performed to evaluate the resin matrix and durability of filler particle. Regarding silane coupling agent, there were several studies about the introduction of new silane coupling agents in order to achieve the more hydrolytic durability of the silane coupling agent layer.[18, 42, 43] Nevertheless, γ-methacryloxypropyltrimethoxysilane (γ-MPTS) is still the popular silane coupling agent

used in dental restorative composite resin.   Silanation process has also been studied to achieve good performance of composite.   These include the amount, pH and heat. Recently, the effect of amount of γ-MPTS deposited on silica surface on durability of composite has been reported that the existence of γ-MPTS is a prerequisite to provide the hydrolytic durability for composite resins.   But the effect of the amount is not strongly affected providing that a certain amount is applied.[55]   Slightly acidity of the solution in hydrolyzing the silane coupling agent was believed to assure the good silanation due to strong siloxane bonding between the filler surface and to decelerate the intermolecular condensation silane coupling agent molecules by of stabilizing the Si-OH moiety. The condensation reaction of silane coupling agent was inhibited in acidic solution and accelerated if dried.[56,57] The use of heat in drying silane coupling agent covering ceramic before bonding to visible light cured resin resulted in the higher shear bond strength.[58] There is widely information of temperature used in treating the filler.[28, 59-63] To date, there is no consensus on proper temperature used in drying filler.

Therefore, it was the objective of this study to evaluate separately the effect of temperature in drying silanated filler and pH of the silanated solution used on hydrolytic durability of experimental composite. It was hypothesized that difference in temperature used in drying filler and different pH of silanated solution had no effect on flexural properties and hydrolytic durability of experimental composite.
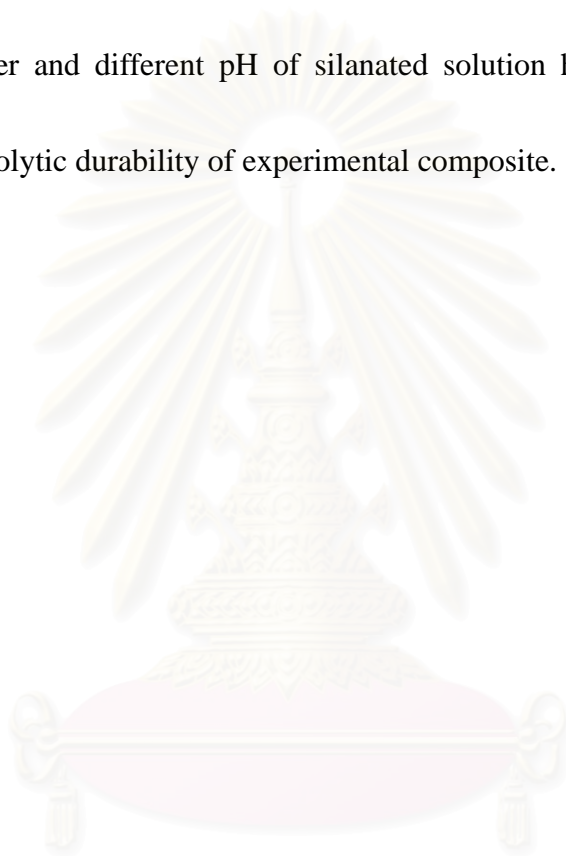
MATERIAL AND METHODS

Silanation of filler:

A spherical-shaped filler (SS15, Osaka Chemical, Osaka, Japan), diameter 1.5 µm, was used in this study. For temperature effect, the filler was silanated at 0.66 mass% using 70 vol% ethanol aqueous solution (The solution was prepared by diluting 95% ethanol (Wako Pure Chemical, Osaka, Japan) with deionized water (Elix 3, Japan Millipore, Tokyo, Japan; pH is around 5.5) at room temperature. Three hours after silanation, the filler was randomly divided into three groups and each was subjected to heating temperature at 50°C, 80°C and 110°C for three hours. After the fillers were cool down to room temperature, they were ready to make composite. For the effect of pH, filler was also silanated with 0.66 mass% with 70% ethanol solution with pH equaled 1, 2, and 4 by adjusting with hydrochloric acid (Merck, German) with deionized water. For control group, the filler was silanated with 0.66 mass% using 70% ethanol solution. After silanation, the filler was left to dry at room temperature for additional 14 days prior to make composite.

Characteristics of silanated filler:

Silanated filler of each group was investigated to understand characteristics of silanated filler by a differential scanning calorimeter (DSC).

Heat flow was monitored during heating approximately 10 mg of fillers using the DSC (DSC3000, Bruker AXS, Yokohama, Japan) at a heating rate of 10°C/minute. Five measurements were carried out for each filler condition. Measured heat flows were analyzed with Dunnett comparison at $p<0.05$.

Silanated filler from each group of heat treatment was dispersed into tetrahydrofurane, THF, (Wako Pure Chemical, Osaka, Japan) and stirred. After stirring, the suspension was centrifuged and supernatant was checked with UV spectrophotometer at 225 nm. The procedure was repeated until the γ-MPTS could not be detected by UV spectrophotometer. The filler was then dried at room temperature and used in TGA.

TGA was performed using TG-DTA2000 (Bruker AXS, Yokohama, Japan) on silanated filler and silanated filler washed with THF under oxygen at a heating rate of 5°C per minute. Each condition was performed twice and averaged.

Composite resin preparation:

The resin matrix of all experimental composite was 70/30 mass% of urethane dimethacrylate (UDMA; Art resin SH-500B, Negami Chemical, Ishikawa, Japan) and triethyleneglycol dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan). Zero point five mass% of camphorquinone (Aldrich Chemical, Milwaukee, Wis) and 1.0 mass% of dimethylaminoethylmethacrylate (Wako Pure Chemical, Osaka, Japan) were used as the photoinitiator and reducing agent, respectively. All materials were used as received without any further purification. The filler loading in all experimental composite resins was kept constant at 65 mass%. One hundred and sixty eight specimens, 24 from each composite, were fabricated from seven experimental composite resins. There were T50, T80 and T110 groups for effect of temperature and pH 1, pH 2 and pH 4 groups for effect of pH while the silanated filler using ethanol solution without adjusting pH at room temperature served as the control for both groups.

Flexural test:

The 2.0 x 2.0 x25.0 mm rectangular specimen was fabricated as suggested in ISO 4049:2000.[31]   The specimen was irradiated using a laboratory light-polymerizing unit (Labolight II, GC, Tokyo, Japan) for 3 minutes from each side of specimen.   The specimen was later kept in the 37°C water.   After 24 hours storage in the incubator at 37°C, six specimens were randomly selected from each group and tested for baseline value at day 0.   The remaining specimens were then placed in the Soxhlet's extractor and subjected to boiling water condition for additional 1, 7, and 28 days.   At the end of each time, six specimens were again randomly selected and tested.   All specimens were subjected to a 3-point bending test in 37°C water using a micro material test machine (MMT-250N, Shimadzu, Kyoto, Japan).   Flexural strength and flexural modulus were obtained from each test using analyzing software (Trapezium II, Shimadzu, Kyoto, Japan).   Each effect was separately analyzed using 2-way ANOVA and all groups were further analyzed with Dunnett comparison.   The statistic significance was considered at $p < 0.05$.

SEM observation:

Fracture surfaces of specimens after the flexural test were gold sputter coated and examined by secondary electron imaging using a scanning electron microscope (Hitachi S-4500, Tokyo, Japan).

RESULT

Figures 5.1 and 5.2 show the flexural strength and flexural modulus of the experiment composites at each storage period. For temperature effect, statistic analysis showed significant differences of two main factors, the temperature factor and storage period, for flexural strength; while flexural modulus showed significant differences of two main factors and the interaction. The flexural strengths of T50 and T80 were significantly greater than that of control and T110 group (Fig 5.3). The flexural strength showed the maximum value at 1 or 7 day storage. The flexural modulus of T110 was significantly greater than that of the control (Fig 5.4). The flexural modulus showed the maximum value at 1 or 7 day storage. Regarding pH effect, there was no significant difference in main factor, pH, on both flexural strength and flexural modulus; however, the significant differences in storage period and interaction were detected. The flexural strength and flexural modulus showed the maximum values after storage.
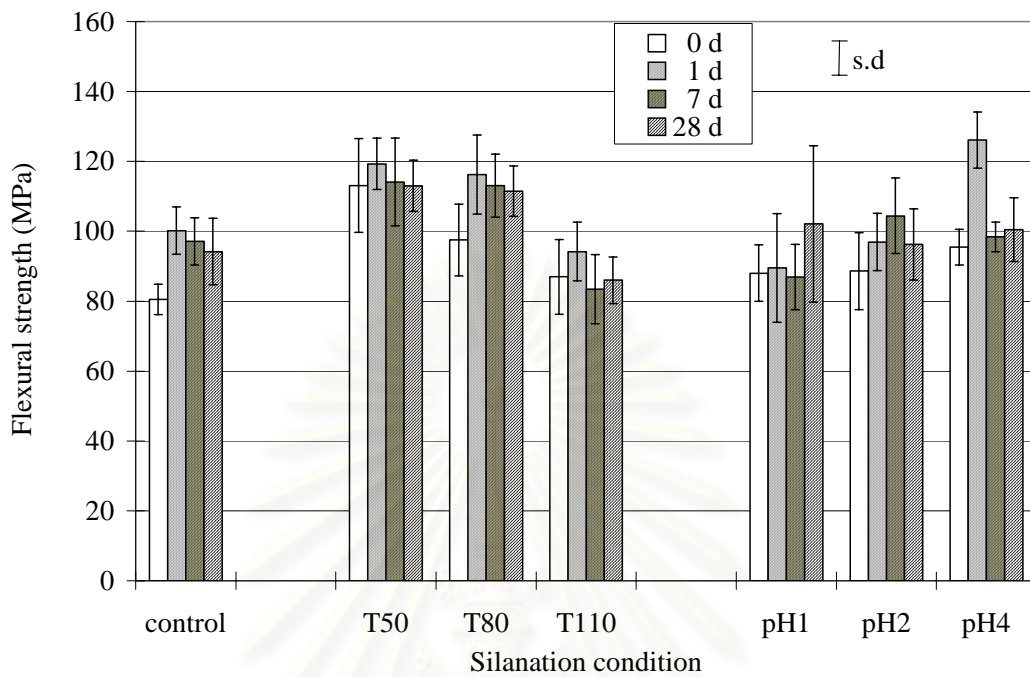
Fig 5.1   Effect of silanation conditions on flexural strength over storage period
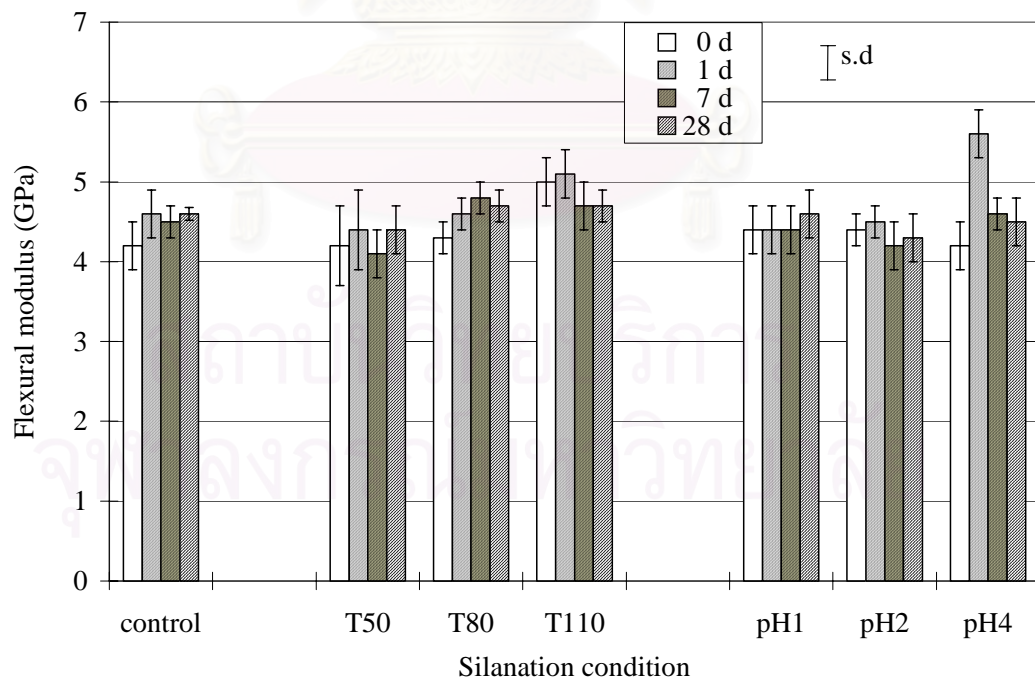
Fig 5.2   Effect of silanation conditions on flexural modulus over storage period
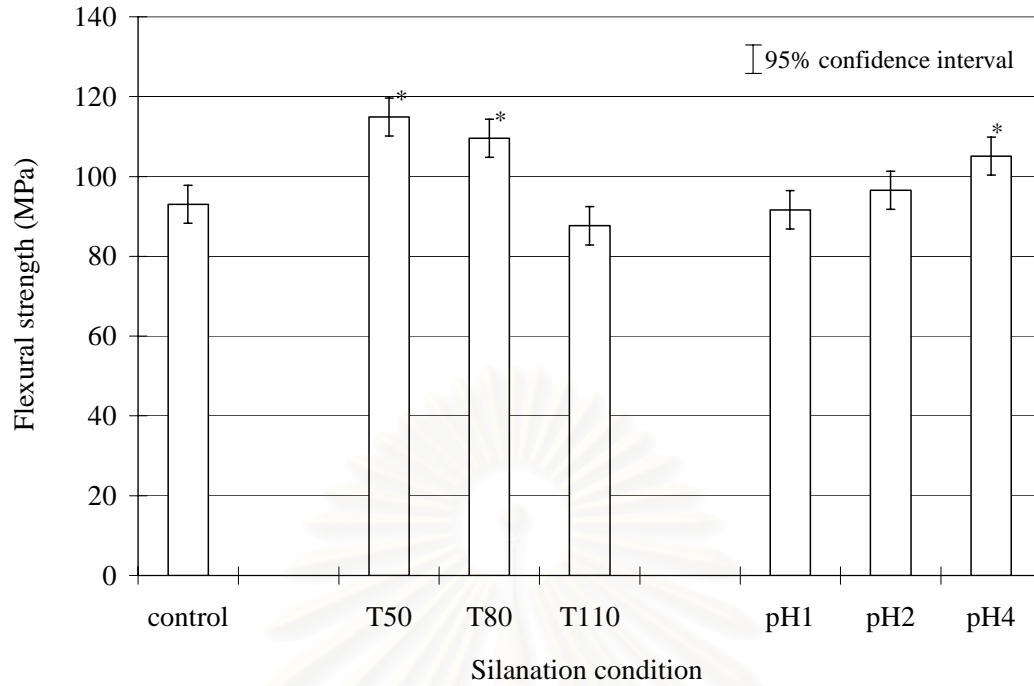
Fig 5.3   Flexural strength of different heating temperature and pH.
Bars with an asterisk were significantly different from the control
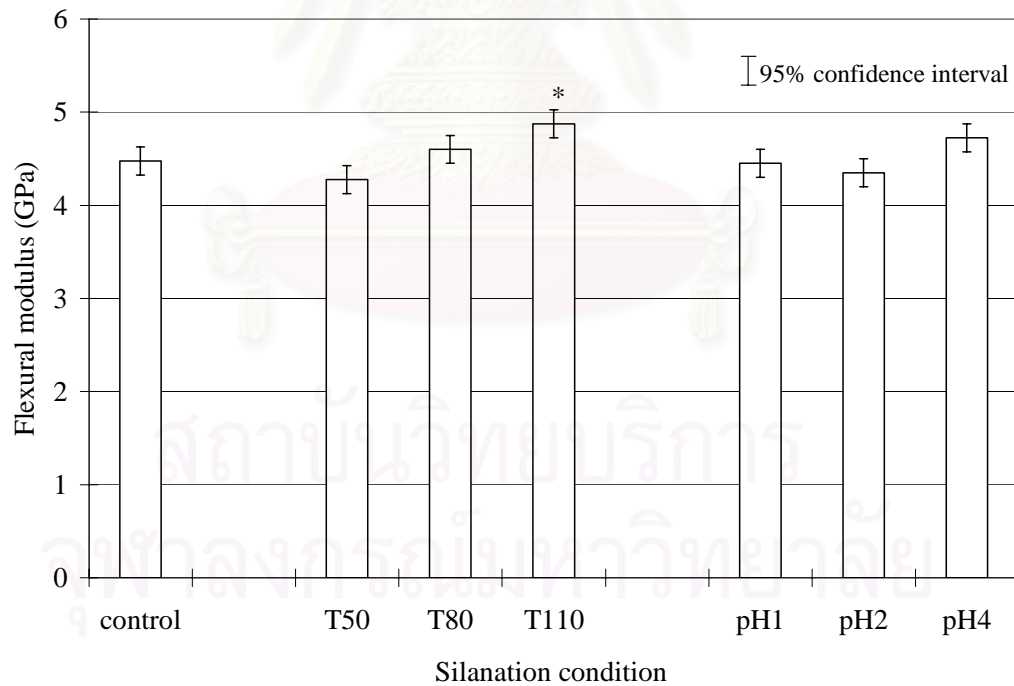
Fig 5.4   Flexural modulus of different heating temperature and pH.
A Bar with an asterisk was significantly different from the control

A broad exothermal peak from 110 to 210ºC was observed from DSC. Amounts of heat flow were exhibited in Fig 5.5. The exothermal heat of the control was approximately 1.2 cal/g, the heat flow significantly decreased with heating treatment, while amounts of heat flow did not change or increased with acidic solutions.
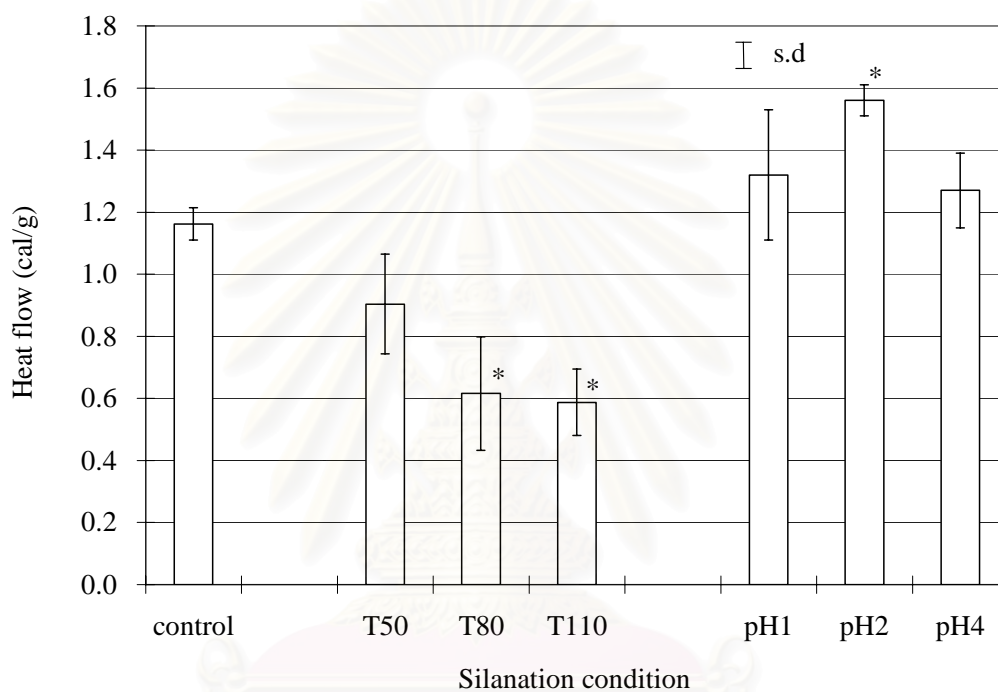
Fig 5.5   Heat flow of fillers with various silanation conditions
Bars with an asterisk were significantly different from the control.

SEM images of fracture surfaces from all groups except T110 showed that the filler surface was covered with matrix resin. However, the fracture surface of T110 showed exposed filler surface and dimple due to filler drop-out, which demonstrated poor bonding between filler and matrix (Fig 5.6).
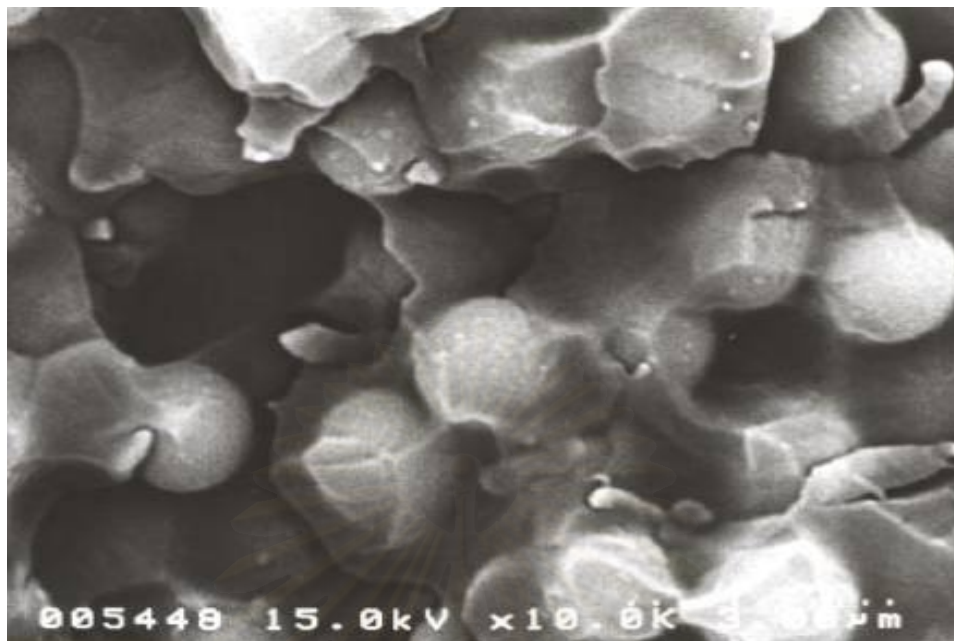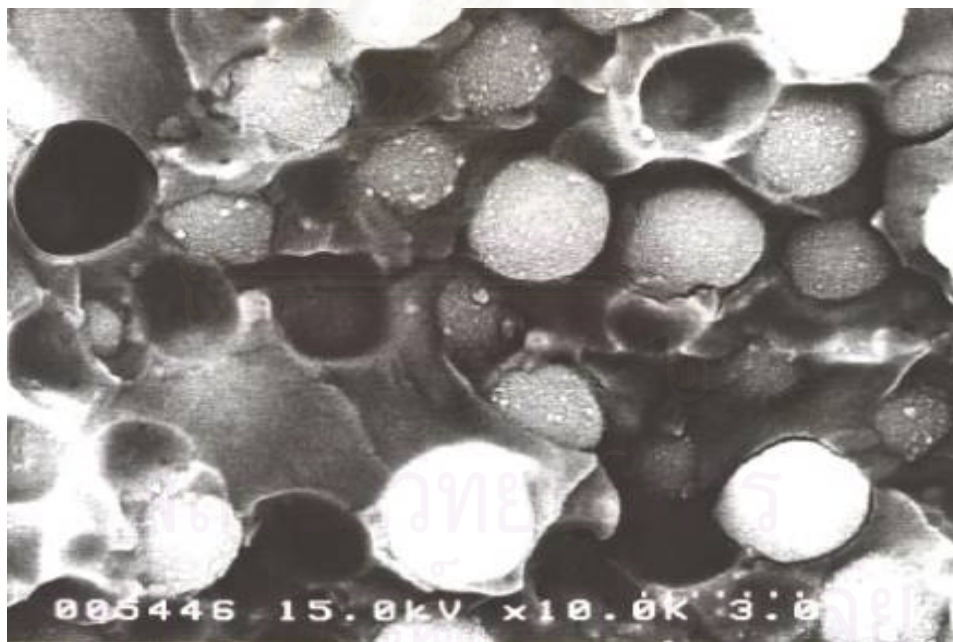
Fig 5.6   Typical SEM images of fracture surfaces. a: T50, b: T110.

The weight loss following TGA of all heat-treated groups and after washing with

THF were ranged from 0.14 ± 0.06 to $0.27 \pm 0.12\%$. These values considered comparable

amount as shown in Fig 5.7.
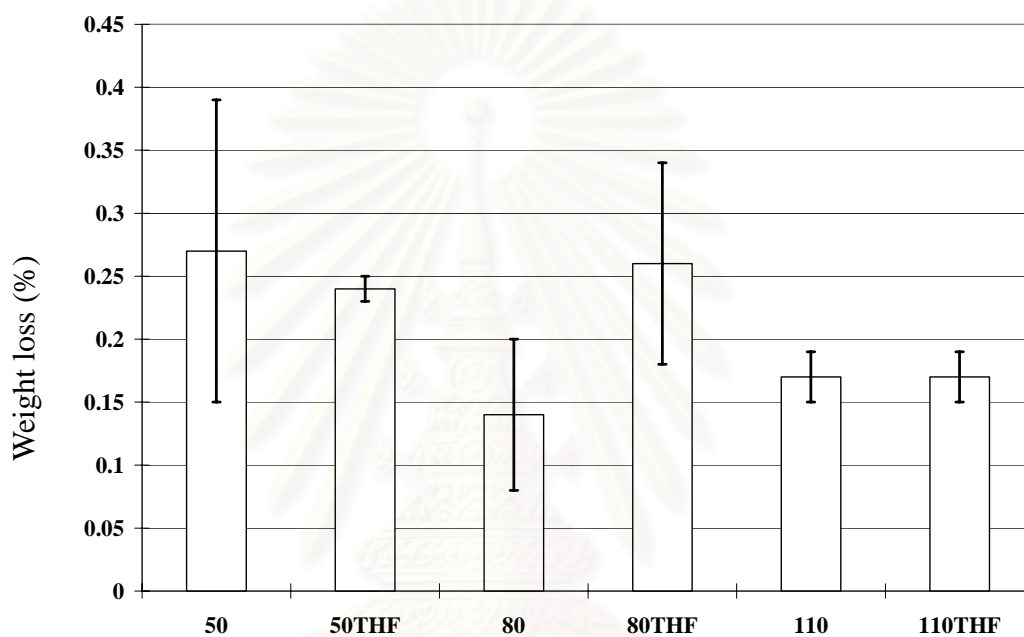
Fig 5.7 The percent weight loss of filler resulted from TGA

DISCUSSION

In this study, spherical shaped silica was used in order to avoid the interlocking effect from the other shape of filler. The result of the study suggested that application of heat less than 80°C for drying filler resulting in better flexural strength. The result from this study is in agreement with Nishiyama et al.[64] The utilization of 110°C in drying silanated filler may promote the condensation and cross-linking among silane coupling agent molecules forming oligomer over chemisorbed silane on the silica surface resulting in inadequate vinyl groups to create bonding to resin matrix. The exothermal heat flow monitored by DSC was considered due to the polymerization of vinyl groups of physisorbed silane coupling agents. The decrease of heat flow with an increase of silanation process temperature suggested that the amounts of physisorbed silane coupling agents decreased with an increase of silanation process temperature. This phenomenon agrees with the previous report.[64] This was also supported by SEM of the fracture surface of 110°C, which showed obviously poor bonding between filler and resin matrix. TGA also confirmed the indifference in amount of silane coupling agent covering filler which excluded the amount effect.

The effect of temperature used in drying filler on flexural modulus was not strongly affected as in flexural strength. The flexural modulus of all groups showed comparable values even with significant differences as shown in statistic analysis. Stiffness may result from postpolymerization of the resin matrix and interlocking effect of filler particle in composite.

From the result of this study, there was no effect of pH on hydrolytic durability of composite on both flexural strength and flexural modulus. According the results of DSC, the amounts of physisorbed silane coupling agents were considered to be equal or increase when the acidic solution was used. Nevertheless, the previous study did not elucidate the effect of pH on silanated solution in terms of mechanical properties and hydrolytic stability of composite. However, this result supported the finding of Naviroj et al [65] that the absorption of γ-MPTS on silica is independent of pH unlike other silane coupling agents. Unlike the temperature effect, the effect of pH, which demonstrated in different molecular weight moieties in adsorption on silica showed no effect on flexural properties and durability of composite. The significant differences in storage period on both flexural strength and modulus which 1 day storage showed greatest value due to the postpolymerization of resin matrix which can also be observed on temperature effect even statistic insignificant.

CONCLUSION

The effects of heat application to the filler and pH on the flexural properties and hydrolytic stability of experimental composites were studied to understand the optimal condition in silanation using γ-MPTS. Within the limitation of this study, it was concluded that heating at 50°C and 80°C increased flexural strength while heat of 110°C and pH showed no effects on flexural properties and durability of composite.

CHAPTER VI

GENERAL DISCUSSION AND CONCLUSION

To clearly understand the result of the study and to test the hypotheses, several techniques and approaches had been made in an attempt to find the optimum procedure in silanating silica filler which yields a better flexural properties and a hydrolytic stable composite resin. It resulted from the previous studies which had shown the degradation of composite resin occurred after long-term water storage. The previous studies had shown that the degradation of composite resin occurred through three main aspects. They are resin matrix, filler and interface between filler and resin matrix. It is believed that effective reinforcement of composite resin in moist environment mainly depended on the stability of interface between two dissimilar materials. Therefore, these investigations were focused only on silane coupling agent, mainly silanation process; amount, heating and pH. Gamma-MPTS is common and effective in silanating filler used in dental resin composite. From the previous pilot studies, it has been shown that γ-MPTS provided experimental composite with an acceptable mechanical properties and hydrolytic durability if the filler was silanated properly; unlike some commercial dental resin composites.

In order to confirm the mechanical properties and hydrolytic durability of resin matrix used in the experimental model. The study in part I was performed to clarify the hydrolytic durability of two resin matrix comomoners. The result indicated that BisGMA/TEGDMA comonomer was hydrolytic unstable. This resulted from the water adsorption of water into the polymer network. The water molecules were bound and

unbound types. The bound type of water is the water at the hydroxy group whilst the unbound is the water molecules in the nanopores, which results from polymerization creating space. TEGDMA is also the hydrophilic monomer. Therefore, it also plays role in water adsorption. To exclude the amount effect of TEGDMA, the ratio of TEGDMA was constantly maintain at 30 mass%. Also, in order to minimize the effect of resin matrix type in following parts, UDMA/TEGDMA was selected as resin matrix in part II and III of this study since it demonstrated the better hydrolytic stability.

In modern composites, several minerals are used in the formula. For example, there are silica, barium, zirconia and quartz, etc. Among these fillers, silica is the main component and widely used in almost all composites. Therefore, silica is selected and employed as the experimental model of the study.

Flexural properties have been selected for evaluation because resin composite shows plastic deformation prior to fracture. Therefore, compressive strength or indirect diametral tensile strength are not appropriate as the parameters used in evaluation composite. Direct tensile is one of the choice but the specimen preparation and alignment prior to the test are very complicated to achieve an accurate represented value. The flexural test also subjects materials in combination modes; upper side of the beam is under compressive mode while lower side of the beam is in tensile mode. The flexural modulus can also be calculated from the slope of the stress and strain curve under elastic deformation. This value represents the stiffness of the material. It means how much material can withstand deformation prior to fracture. In order to observe the mode of failure and to simplify the model for interpretation, spherical-shaped silica filler was selected in the experiments. The filler used in these studies is very uniformed in size as

shown in the SEM image in previous chapter. This provides a simple model in interpretation of the fracture surface because the interlocking effect of the filler in rein composite has been eliminated and uniformed silanation can also be achieved. The 1.5μm spherical shaped filler was selected following the previous study, which, showed that filler size 1.3-1.5μm, provided composite with the high mechanical coherence.[66]

There were several methods in the literature utilizing in accelerating degradation of resin composite. Among the several methods, immersion in Soxhlet's extractor used in this study has been shown to cause degradation of both experimental and commercial composites effectively. The water circulating in the chamber is always distilled water and the temperature in the chamber is very stable during operation.

Since the siloxane bonding between the silane coupling agent and silica is reversible after reaching equilibrium, therefore, flexural properties were obtained from testing the materials in the 37°C. This equilibrium is also very sensitive with hydration and dehydration. In order to prevent dehydration and rehydration, the materials were handled in the 100% humidity by all times.

To understand the characteristics of silanated filler, FTIR, thermogravimetric analysis, differential scanning calorimeter and organic element analysis were used in this study.

The FTIR is an important technique in organic chemistry. It is a method to identify the presence of certain functional groups in a molecule. It is also used the unique collection of adsorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Spectra of organic compounds have two general areas: The fingerprint region, peaks in this region arise from complex deformations of the

molecule. They may be characteristic of molecular symmetry, or combination bands arising from multiple bonds deforming simultaneously. The functional group region, peaks in this region are characteristic of specific kinds of bonds, and therefore can be used to identify whether a specific functional group is present. In this study, FTIR was used to check the existence of γ-MPTS molecule coated on silica surface in chapter IV. The interested regions are the C-H and C=O vibration peaks which represent the silane molecule on silica. The quantitative characteristic can hardly be achieved through FTIR because only absorbance or transmittance was reported, rather, it is more a qualitative method. Therefore, a more accurate approach such as thermogravimetric analysis and organic elemental analyis were further used in finding the silane amount adsorbed on the silica surface.

The thermogravimetric analysis (TGA) allows one to determine oxidation or reaction kinetics of materials such as ceramics, metals and polymers. TGA monitors the weight change during heating application of the sample as a function of time and temperature compared to standard such as alumina. It is a method in chemistry to elucidate the substance deposited on the material or check the purity of specimen or to characterize phenomena such as evaporation and drying, decomposition, oxidation, and oxidative stability. This study utilized this technique to quantify the amount of γ-MPTS deposited on silica surface. The results from the TGA in chapter V showed that heating effect did not cause any differences in the silane amount absorbed on the filler. Results obtained from TGA also confirmed at least two types of silane adsorbed on silica surface. However, DTA (Differential Thermal Analysis), which also recorded concurrently with TGA suggested perhaps there was possibly another chemisorption layer of which very

stable. TGA has provided useful information in elucidating the amount of adsorbate deposited on substrate. Future studies on this deposited layer are needed to clarify this issue.

The differential scanning colorimeter (DSC) measures the heat flow to and from the sample as a function of temperature. Various materials characteristics can be determined from these data, including oxidative stability, purity, and polymorphism. Chemical reactions, melting behavior, and the temperature evolution of the specific heat can also be investigated. DSC offers a comparatively facile and rapid method for determining the degree of conversion of vinyl group. The heat flow was measured by DSC in chapter V in order to demonstrate the unreacted silane coupling agent. As a result, heating temperature of silanation affected the amounts of unreacted silane which is believed to be the physisorbed silane.

The organic elemental analysis determines amounts of organic elements such as hydrogen, carbon, oxygen and nitrogen by measuring the weight of these elements during heating. It is performed to characterize and /or to prove the elemental composition of an organic specimen. Therefore, the amount of adsorbate deposited on substrate can be calculated based on molecular weight of the substance. The drawback of this apparatus in this study was that the detection limit of the apparatus concealed the small change of the silanation amount because the amounts of organic components of filler are relatively small. The detection limit for carbon and nitrogen at sample amounts of 2-3 mg was found to be at about 0.05 wt% (500 ppm) in what case the uncertainty stays at about 0.02 wt%. With very carbon rich samples the tolerance was slightly exceeded but still within

0.5 wt%. Nevertheless, such a very sensitive apparatus could detect most of the silanated amounts in this study.

From the aforementioned methods, it could be confirmed at this moment that silane species adsorbed on silica surface had at least two types; chemisorbed and physisorbed silane species. The silane molecules will slowly adsorb on silica surface until reaching saturated then excess silane, physisorbed, will lie on chemisorbed silane layer. This characteristic had been clearly demonstrated in chapter IV on the effect of the different amount. Since drying period after silanation was 14 days prior to mix with resin matrix, therefore, saturated chemisorption can be anticipated. The use of heating in drying filler which can reduce the 14 days drying time has been proven as a promising method in providing a better mechanical properties and a more hydrolytic durability of composite with the aids of heating temperature less than 80˚C. From the SEM images, it was clearly proven that the application of heating over 80˚C would hasten the condensation among silane molecules, which resulted in less vinyl groups to create bonding with resin matrix. The Si-OH group is stable in the silanated solution. This phenomenon has been shown in the chapter IV that the chemisorbed amount increases until saturation and yields a very hydrolytic stable composite; otherwise, the hydrolytic degradation will arise. The application of heating to dry silanated filler is to provide a very stable siloxane bond between the filler and silane molecule. But in this study, it had been shown that over-heating promotes the condensation of the silane molecule and forced cross linking thus vinyl groups on silane molecules are utilized on polymerization among silane molecule and resulted in inadequate double bond in polymerized with resin

matrix. This phenomenon has been clearly demonstrated from DSC on the different of calories used in oxidized filler among three temperatures used in this study.

It has been clearly shown in chapter IV that the silanation amount was not sensitive in providing composite with better mechanical properties and hydrolytic durability. However, the silane molecule covering filler is a requirement to yield a better mechanical properties and hydrolytic stable. Slightly excess silanation calculated based on BET surface area and wetting ability of silane has been proposed in this study because silane molecules can form a bi-layer. Even though, the significance of the hydrolytic stability could not be detected; the results had shown some trend toward this proposed statement. The different amount had provided the composite with slightly different mechanical properties therefore in manufacturing composite resin; manufacturer can utilize this result in tailor composite as desire.

Regarding the effect of temperature, it is advised that application of heat less than 80°C in drying silanated filler rendered a better composite. This has been confirmed by SEM image and DSC that the available of vinyl group in silane molecule is important in creating a better bonding with resin matrix. It is interesting that the different in pH had no effect on composite even though slightly acidity has been believed to create a better environment in silanation. Low pH or high acidity can promote the hydrolysis of silane molecule in the presence of water. High molecular weight species of silane molecule was believed to provide better composite. But the result from this study cannot be drawn to support this theory. Contrarily, the result supported another school of thought that the adsorption of γ-MPTS is independent of pH.

The future study on morphology and adsorption behavior of γ-MPTS deposited on silica surface by TOF-SIM (Time of Flight-Secondary Ion Mass Spectrometry) may provide an in depth information in order to clarify the issue. There are also other minerals that are currently used in the composite such as barium glass, strontium glass and Zirconia etc. The effect of silanation on other types of filler is also required in order to have a clear picture on silanation. Decontamination of filler prior to silanation effect on mechanical properties is also recommended.
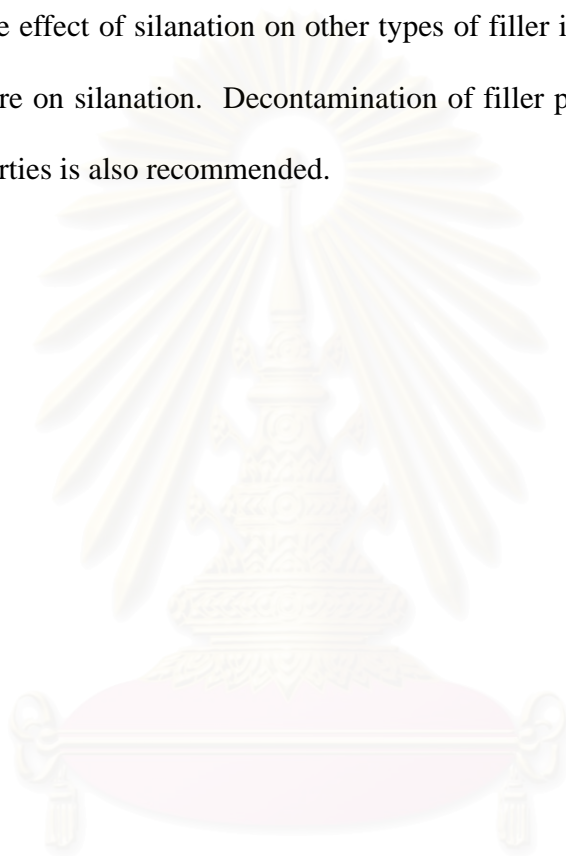
Conclusion

Within the limitation in the present studies, the following conclusion can be drawn:

1. UDMA/TEGDMA combination is a more hydrolytic durable resin matrix than BisGMA/TEGDMA.

2. In the silanation process, the amount of silanation is not sensitive in providing a better composite resin with hydrolytic durability if a certain amount of silanation is applied. The amount of silanation even a small amount can be able to protect composite from hydrolytic degradation.

3. The use of heating at different temperature level yields different mechanical properties of composite with different hydrolytic stability. The application of heating more than 80°C has an adverse effect on mechanical properties and hydrolytic durability of composite. This causes by the inadequate vinyl groups available for create the covalent bond with resin matrix.

4. The acidity of silanation solution used in silanating filler has no effects on mechanical properties and hydrolytic durability.

REFERENCES

1. Bowen, R. L. Effect of particle shape and size distribution in a reinforced polymer. <u>J Am Dent Assoc</u> 69 (1964): 481-95.

2. Antonucci, J. M.; and Stansbury, J. W. Molecularly designed dental polymers. In: Arshady R, editor. Desk reference of functional polymers: syntheses and applications. <u>American Chemical Society Publication</u>; (1997): 719-38.

3. Geurtsen, W., and Leyhausen, G. Chemical-biological interactions of the resin monomer triethylene glycol dimethacrylate (TEGDMA). <u>J Dent Res</u> 80 (2001): 2046-50.

4. Schafer, T. E., Lapp, C. A., Hanes, C. M., Lewis, J. B., Wataha, J. C., and Schuster, G. S. Estrogenicity of bisphenol A and bisphenol A dimethacrylate in vitro. <u>J Biomed Mater Res</u> 45 (1999): 192-197.

5. Li, Y., Swartz, M. L., Phillips, R. W., Moore, B.K., and Roberts, T.A. Effect of filler content and size on properties of composites. <u>J Dent Res</u> 64 (1985): 1396-1401.

6. Ferracane, J. L., Matsumoto, H., and Okabe, T. Time-dependent deformation of composite resins- Compositional consideration. <u>J Dent Res</u> 64 (1985): 1332-1336.

7. Braem, M., Finger, W, Van Doren, V. E., Lambrechts, P., and Vanherle, G. Mechanical properties and filler fraction of dental composites. <u>Dent Mater</u> 5 (1989): 346-349.

8. Calais, J.G., and Soderholm, K. J. M. Influence of filler type and water exposure on flexural strength of experimental composite resin. <u>J Dent Res</u> 67 (1988): 836-840.

9. Tarumi, H., Torii, M., and Tsuchitani, Y. Relationship between particle size of barium glass filler and water sorption of light-cured composite resin. <u>Dent Mater J</u> 14 (1995): 37-44.

10. Miyasaka, T. Effect of shape and size of silanated fillers on mechanical properties of experimental photo cure composite resins. <u>Dent Mater J</u> 15 (1996): 98-11.

11. Miyasaki, T., and Yoshida, T. Effect of binary and ternary filler mixtures on the mechanical properties of composite resins. <u>Dent Mater J</u> 19 (2000): 229-244.

12. Plueddemann, E. P. <u>Silane coupling agent</u>. New York: Plenum Press, 1991.

13. Denoyel, R., and Trens, P. Influence of water on adsorption of triethylsilanol onto silica. <u>J Phys Chem</u> 99 (1995): 3711-3714.

14. Osterholtz, F. D., and Pohl, E. R. Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes. <u>J Adhesion Sci Technol</u> 6 (1992): 127.

15. Mohsen, N. M., and Craig, R. G. Effect of silanation of fillers on their dispersability by monomer systems. <u>J Oral Rehab</u> 22 (1995): 183-189.

16. Mohsen, N. M., and Craig, R. G. Hydrolytic stability of silanated zirconia-silica-urethane dimethacrylate composites. <u>J Oral Rehab</u> 22 (1995): 213-220.

17. Craig, R. G. and Dootz, E. R. Effect of mixed silanes on the hydrolytic stability of composites. <u>J Oral Rehab</u> 23 (1996): 751-756.

18. Nihei, T., Kurata, S., Kondo, Y., Umemoto, K., Yoshino, N., and Teranaka, T. Enhanced hydrolytic stability of dental composites by use of fluoroalkyltrimethoxysilanes. J Dent Res 81 (2002): 482-486.

19. Yang, R., Liu, Y., Wang, K and Yu, J. Characterization of surface interaction of inorganic fillers with silane coupling agents. J. Anal. Appl. Pyrolysis. 70 (2003): 413-425.

20. Nishiyama, N., Shick, R., and Ishida, H. Adsorption behavior of a silane coupling atgent on colloidal silica studied by gel permeation chromatography. J Colloid Interface Sci 143 (1991): 146-156.

21. Nishiyama, N., Horie, K., Shick, R., and Ishida, H. Influence of adsorption behaviour of a silane coupling agent onto silica on visco-elastic properties. Polymer Communications 31 (1990): 380-379.

22. Soderholm, K. J. M., and Shang, S.W. Molecular orientation of silane at the surface of colloidal silica. J Dent Res 72 (1993): 1050-1054.

23. Nishiyama, N., Komatsu, K., Fukai, K., and Nemoto, K. Influence of adsorption characteristics of silane on thehyrolytic stability of silane at the silica-matrix interface. Composites 26 (1995): 309-313.

24. Nishiyama, N., Nagashima, M., Nemoto, K., Suzuki, K., and Kumagai, M. The effect of heat-treatment on the adsorption behavior of silane coupling agent. Proceedings of ICCM-10 1995: 565-572.

25. Liu, Q., Ding, J., Chambers, D. E., Debnath, S., Wunder, S. L., and Baran, G. R. Filler-coupling agent-matrix interactions in silica/polymethylmethacrylate composites. J Biomed Mater Res 57 (2001): 384-393.

26. Shirai, K., Yoshida, Y., Nakayama, Y., Fujitani, M., Shintani, H., Wakasa, K., Okazaki, M., Snauwaert, J., and Van Meerbeek, B. Assessment of decontamination methods as pretreatment of silanization of composite glass fibers. J Biomed Mater Res 53 (2000): 204-210.

27. Lim, B. S., Ferracane, J. L., Condon, J. R., and Adey, J. D. Effect of filler fraction and fillersurface treatment on wear of microfilled composites. Dental Materials 18 (2002): 1-11.

28. Santos, C., Luklinska, Z. B., Clarke, R. L.,Davy, K. W. M. Hydroxyapatite as a filler for dental composite materials: mechanical properties and in vitro bioactivity of composites. J Mater Sci:Mater Med 12 (2001): 565-573.

29. Santos, C., Clarke, R. L., Braden, M., Guitian, F., and Davy, K. W. M. Water absorption characteristics of dental composites incorporating hydroxyapatite filler. Biomaterials 23 (2002): 1897-1904.

30. Xu, H. H. K., Quinn, J. B., Smith, D. T., Antonucci, J. M., Schumacher, G. E., and Eichmiller, F. C. Dental resin composite containing silica-fused whiskers-effects of whisker-to-silica ration on fracture toughness and indentation properties. Biomaterials 23 (2002): 735-742.

31. ISO 4049: Dental resin-based restorative materials. Geneva, International Organization for Standardization 2000.

32. Asmussen, E., and Peutzfeldt, A. Influence of UEDMA, BisGMA and TEGDMA on selected mechanical properties of experimental rein composites. Dent Mater 14 (1998): 51-56.

33. Indrani, D. J., Cook, W.D., Televantos, F., Tyas, M. J.., and Harcourt, J. K. Fracture toughness of water-aged resin composite restorative materials. Dent Mater 11 (1995): 201-207.

34. Yiu, C.K.Y., King, N.M., Pashley, D.H., Suh, B.I., Carvalho, R.M., Carrilho, M.R.O., Tay, F.R. Effect of resin hydrophylicity and water storage on resin strength. Biomaterials (in press)

35. Musto, P., Ragosta, G., Scarinza, G., Mascia, L. Probing the molecular interactions in the diffusion of water through epoxy and epoxy-bismaleimide networks. J Polymer Sci Part B: Polym Phys 40 (2002): 922-938.

36. Ferracane, J.L., Hopkin, J.K. and Condon, J.R. Properties of heat-treated composites after aging in water.   Dent Mater 11 (1995): 354-358.

37. Ferracane, J.L., Berge, H.X. and Condon, J.R.: In vitro aging of composites in water-Effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res 42 (1998): 465-472.

38. Soderholm, K.J. Degradation of glass fiber in experimental composites. J Dent Res 60 (1981): 1867-1875.

39. Soderholm, K.J., Zigan, M., Ragan, M., Fischlschweiger, W. and Bergman, M. Hydrolytic degradation of dental composite resin. J Dent Res 63 (1984): 1248-1254.

40. Pillar, R.M., Smith, D.C. and Maric, B. Fracture toughness of dental composites determined using short-rod fracture toughness test. J Dent Res 65 (1986): 1308-1314.

41. Ferracane, J.L., and Marker, V.A. Solvent degradation and reduced fracture toughness in aged composites. J Dent Res 71 (1992): 13-19.

42. Tanioka, Y., and Nishiyama, N. Influence of the number of silicone functional groups in silane coupling agents on the surface treatment of silica filler. J J Dent Mater 6 (1987): 737-746. (in Japanese)

43. Nishiyama, N., Ishizaki, T., Horie, K., Tomari, M. and Someya, M. Novel polyfunctional silanes for improved hydrolytic stability at the polymer-silica interface. J Biomed Mater Res 25 (1991): 213-221.

44. Wang, D., and Jones, F.R. TOF SIMS and XPS studies of the interaction of silanes and matrix resins with glass surfaces. Surf Interface Anal 20 (1993): 457-467.

45. Arkles, B. Silane Coupling Agent Chemistry, Petrarch Systems Catalogue, Bristol, Pennsylvania, 1987, 59 pp.

46. Wood, D.L., Rabinovich E.M., Johnson D.W., Mc Chesney J.B., Vogel E.M.   J Am Ceram Soc 66 (1983): 693-699.

47. Miller, J.D., Ishida, H. Quantitative monomolecular coverage of inorganic particulates by methacryl-functional silanes. Surf Sci 148 (1984): 601-622.

48. Nishiyama, N., Katsuki, H. and Horie, K. Adsorbed behavior of spin-labeled silane coupling agent on colloidal silica studied by electron spin resonance. J Biomed Mater Res 21 (1987): 1029-1038.

49. Wang, D., and Jones, F.R. TOF SIMS and XPS study of the interaction of silanized E-glass with epoxy resin. J Mater Sci 28 (1993): 1396-1408.

50. Yamamoto, M., and Takahashi, H. Tensile fatigue strength of light cure composite resins for posterior teeth. Dent Mater J 14 (1995): 175-184.

51. Vijayaraghavan, T.V., and Hsiao, J. Flexural behavior of visible light-cured composites as function of temperature under water immersion test conditions.

Dent Mater 10 (1994): 347-52.

52. Manhart, J, Kunzelmann, K.H., Chen, H.Y., and Hickel, R. Mechanical properties and water behavior of light cured packable composite resin. Dent Mater 16 (2000): 33-40.

53. Santerre, J.P., Shajii, L, and Tsang, H. Biodegradation of commercial dental composite by cholesterol esterase. J Dent Res 78 (1999): 1459-1468.

54. Shin, M.A., and Drummond, J.L. Evaluation of chemical and mechanical properties of dental composites. J Biomed Mater Res 48 (1999): 540-545.

55. Arksornnukit, M., Takahashi, H., and Nishiyama, N. Effects of silane coupling agent amount on mechanical properties and hydrolytic durabilities of composite resin after hot water storage. Dent Mater J 23 (2004): 31-36

56. Nishiyama, N., Asakura, T., and Horie, K. The Infuence of Hydrochloric Acid on the Condensation Behavior of A Silane Coupling Agent Studied by 29Si NMR. Reports on Progress in Polymer Physics in Japan 29 (1986): 563-566.

57. Nishiyama, N., Shick, R., and Ishida, H. Adsorption behavior of a silane coupling agent on colloidal silica studied by gel permeation chromatography. J Colloid Interface Sci 143 (1991): 146-156.

58. Roulet, J.F., Soderholm, K.J.M., and Longmate, J. Effects of treatment and storage conditions on ceramic/composite bond strength. J Dent Res 74 (1995): 381-387.

59. Nakabo, S., Torii, Y., Itota, T., Ishikawa, K., and Suzuki, K. Regulation of NaF release from BisGMA/TEGDMA resin using gamma-methacryloxypropyltrimethoxysilane. Dent Mater 18 (2002): 81-87.

60. Halvorson, R.H., Erickson, R.L., and Davidson, C.L. The effect of filler and silane content on conversion of resin-based composite. Dent Mater 19 (2003): 327-333.

61. Yoshida, Y., Shirai, K., Shintani, H., Okazaki, M., Suzuki, K., and Van Meerbeek, B. Effect of presilanization filler decontamination on aesthetics and degradation resistance of resin composites. Dent Mater J 21 (2002): 383-95.

62. Debnath, S., Wunder, S.L., McCool, J.I., and Baran, G.R. Silane treatment effects on glass/resin interfacial shear strengths. Dent Mater 19 (2003): 441-448.

63. Liu, Q., Ding, J., Chambers, D.E., Debnath, S., Wunder, S.L., and Baran, G.R. Filler-coupling agent matrix interactions in silica/polymethylmethacrylate composites. J Biomed Mater Res 57 (2001): 384-393.

64. Nishiyama, N., Nagashima, M., Nemoto, K., Suzuki, K., and Kumagai, M. The effect of heat-treatment on the adsorption behavior of silane coupling agent. Proceeding of ICCM-10. Whistler, B.C., Canada 5 (1995): 565-572.

65. Naviroj, S., Culler, S.R., Koenig, J.L., and Ishida, H. Structure and adsorption characteristics of silane coupling agents on silica and E-glass fiber; Dependence on pH. J Colloid Interface Sci 97 (1984): 308-317.

66. Venhoven, B.A.M., deGee, A.J., Werner, A. and Davidson, C.L. Influence of filler parameters on the mechanical coherence of dental restorative resin composites. Biomaterials 17 (1996): 735-740.

VITA

Mansuang Arksornnukit, a son of Mr. Boonrak and Mrs. Malee, was born in Bangkok in October 1961. He was married to Dr. Wasana. He began his elementary and high school education from Bangkok High School, and Triam Udom Suksa, respectively. He received Doctor of Dental Surgery degree with Honors from Chulalongkorn University in 1986. He received further advanced education at State University of New York at Buffalo during 1986-1988 and 1989-1990. After obtaining the certificate of Prosthodontics from State University of New York, he further his clinical training in Maxillofacial Prosthetics at Eye and Ear Hospital of Pittsburgh, University of Pittsburgh, Pennsylavania for one year and was awarded certificate in 1989. Upon finishing his clinical training, he worked as the clinical instructor at Department of Prosthodontics, School of Dental Medicine, State University of New York at Buffalo during 1989-1990 concurrently with his work toward Master of Science degree in Biomaterials. He graduated with his M.S. degree from State University of New York at Buffalo in February 1990. He then returned to motherland and started working with Chulalongkorn University, Faculty of Dentistry, Department of Prosthodontics, since July 1990. He was appointed as the assistant professor in 1999.