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Final Report

On

**“Comparison of Titanium Dioxide/Silicon
Dioxide/Zirconium Dioxide Synthesized via Sol-gel
Process to Be Used As Lens Protection”**

By

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ABSTRACT

Many hard coating materials have been developed and based on the use of metal alkoxide or organosiloxanes prepared via the sol-gel process. Titanium glycolate, zirconium glycolate and silatrane precursors were processed as hard coating materials for polyurethane lens. These precursors are inexpensive and the preparation reaction is simple and straightforward. The effects of the sol-gel process parameters, viz. the type of precursors, the solvent, the coupling agent (GPTS), and the curing agent (3-APS) were investigated. The surface property evaluation of ophthalmic lens was conducted with respect to the scratch resistance, the adhesion by the tape test, the immersion in boiling water, the refractive index, the %light transmission. The coating solutions were applied onto the polyurethane substrate to achieve the film thickness of $\sim 5.0 \mu\text{m}$, at the optimized concentration. Silatrane has a good property using the formula of precursor:HCl:IPA:GPTS:%APS (by volume) equal to 0.05g:600 μL :1000 μL :600 μL :5%. The same condition was applied for the zirconium glycolate precursor. On the other hand, the titanium glycolate precursor was found to have the optimal formula of 0.05g:600 μL :1000 μL :600 μL :4%. The scratch line results at the coated polyurethane are superior when compared with that of the uncoated polyurethane. When compared with the commercially hard coating lens, the results are nearly the same.

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บทคัดย่อ

สารเคลือบแข็งจำนวนมากได้ถูกพัฒนาขึ้นมาจากสารประกอบของโลหะอัลคอกไซด์ หรือสารประกอบอินทรีย์ไฮลอกเซน โดยเตรียมผ่านกระบวนการ ไซล-เจล สารตั้งต้นโททานเนียมไกลโคเลต เซอร์โคเนียมไกลโคเลต และซิลาทเรน ได้ถูกนำไปประยุกต์ใช้ในงานเคลือบแข็งผิวเลนส์ชนิดโพลียูรีเทน เนื่องจากสารตั้งต้นเหล่านี้สังเคราะห์ง่ายและราคาถูก การศึกษาได้มีการมุ่งประเด็นไปที่ผลกระทบที่เกิดกับสมบัติของเลนส์หลังจากถูกเคลือบแข็ง โดยตัวแปรที่ได้ศึกษา ได้แก่ ชนิดของสารตั้งต้น ตัวทำละลาย สารเชื่อมต้อ (GPTS) และสารเร่งการแข็งตัว(3-APS) การประเมินสมบัติของพื้นผิวของเลนส์กระทำได้ด้วยการทดสอบการทนรอยขีดข่วน ความสามารถในการยึดติดผิวด้วยการดึงเทปกาว การดัมพ์ชิ้นงานในน้ำเดือด การตรวจสอบความสามารถในการหักเหแสง และการหาค่าความสามารถในการส่องผ่านของแสง

สารเคลือบแข็งที่เตรียมขึ้นหลังจากเคลือบชิ้นงานมีความหนาประมาณ 5.0 ไมครอน อัตราการผสมที่เหมาะสมที่สุดสำหรับสารละลายที่มีซิลาทเรน หรือเซอร์โคเนียมไกลโคเลตคือ ซิลาทเรน หรือ เซอร์โคเนียมไกลโคเลตปริมาณ 0.05 กรัม ต่อกรดไฮโดรคลอริกที่มีความเข้มข้น 1 โมลาร์ ปริมาณ 600 ไมโครลิตร ต่อไอโซโพรพิลแอลกอฮอล์ปริมาณ 1000 ไมโครลิตร ต่อสารเชื่อมต้อปริมาณ 600 ไมโครลิตร ต่อสารช่วยเร่งการแข็งตัวปริมาณ 5 เปอร์เซ็นต์ โดยปริมาตรของสารผสม สำหรับโททานเนียมไกลโคเลต ส่วนผสมที่ดีที่สุดคือ โททานเนียมไกลโคเลตปริมาณ 0.05 กรัม ต่อกรดไฮโดรคลอริกที่มีความเข้มข้น 1 โมลาร์ ปริมาณ 600 ไมโครลิตร ต่อ ไอโซโพรพิลแอลกอฮอล์ปริมาณ 1000 ไมโครลิตร ต่อสารเชื่อมต้อปริมาณ 600 ไมโครลิตร ต่อสารช่วยเร่งการแข็งตัวปริมาณ 4 เปอร์เซ็นต์ โดยปริมาตรของสารผสม การเคลือบสารตั้งต้นทั้งสามชนิดบนเลนส์ ให้ผลการตรวจสอบที่คิดว่าเมื่อเทียบกับเลนส์ที่ไม่ได้เคลือบ และเมื่อเทียบกับเลนส์ที่เคลือบแข็งในอุตสาหกรรม ให้ผลการทดสอบที่ใกล้เคียงกัน

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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Chapter I

Background and Literature Survey

Introduction

During the early part of this century, the greatest advantages in ophthalmics were related to new kind of lens materials. With the expansion of organic and synthetic polymer chemistry in the 20th century, it was discovered that optically clear materials could be made from polymers. Plastic lens has been used widely due to its lightness and toughness with a slight disadvantage of low scratch resistance. This disadvantage can be eliminated by the hard coating of organometallic polymers onto the lens's surface. In addition, the coated layer also acts as a transition and adhesion promotion layer between the organic substrate and the inorganic anti-refraction layer package. The most important issue regarding the use of hard coating materials is the matching in refractive index with the lens, since the severe interference fringes can be observed from the refractive index mismatched [1].

The sol-gel method is one of the most widely used techniques for the synthesis of various functional coating films. It possesses a number of advantages over conventional film formation techniques, including relatively low processing temperature, ease of coating homogeneous multicomponent oxide films over large surfaces, and good control of the composition and property of the final material. In generally, inorganic/organic hybrid network materials are prepared by the sol-gel process of the starting inorganic material, such as silicon, aluminum, titanium or zirconium metal alkoxides with organic compounds [2-4].

In a previous study [5], a series of organic components included aromatic diol, 3,3'-iminobispropylamine (IMPA), resorcinol (RSOL), diethylenetriamine (DETA) and oligomeric species of poly(ethylene imine) (PEI) have been investigated. The metal alkoxides were tetraethoxysilane (TEOS) and tetramethoxy silane (TMOS) functionalized by 3-isocyanatopropylamine. They have been processed by the sol-gel method. One way of increasing the cross-link density, thereby obtaining stronger interaction

between the inorganic and organic components, is to use functionalized silanes (coupling agents) as cross-linkers. For epoxy/silica hybrid systems the coupling agent, 3-glycidoxypropyl-trimethoxysilane (GPTMS), is a useful molecule [6] while the mixture of triethoxysilylated diethylenetriamine (f-DETA) and tetramethoxysilane [TMOS] was modified by reacting with 3-aminopropyltriethoxysilane (3-APS) [5]. The size distribution of the different inorganic segments in the hybrid materials was very important for specific optical applications. To increase the refractive indices of hard coating materials, the inorganic compounds, such as titania, which has a high optical index of roughly 2.25 (depending on a number of factors) [7-8] and zirconia showed significant improvement in refraction [9]. They can be mixed into the low index coating material using small enough amount not to be optically actives [6].

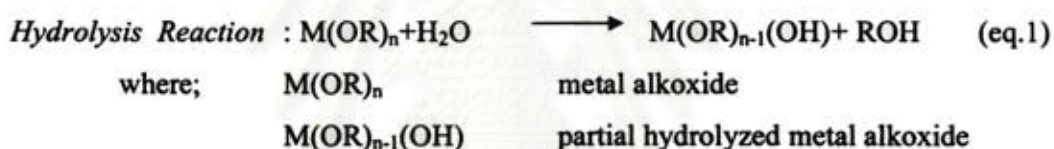
With the effect mankind has had on the environment, water-based polymer coating materials are attracting more and more attention because they can replace harmful solvent-based coating materials in such areas as paints, adhesives and ink, and, hence, can reduce volatile organic compounds to a minimum [10]. Nanocomposite coating materials prepared by the sol-gel process are usually solvent based systems due to the typical sol-gel reaction conditions and have been successfully used in large scale coating technologies for transparent plastics. Typical solvents in the coating systems are methanol and ethanol; they are not desired for ecological, health and safety reasons. In order to bring these results into an application, the storage stability of the water based material was investigated, by ^{29}Si -NMR and viscosity analyses [11]. One of the most widely applied organo-functional alkoxysilanes is GPTMS. Its epoxy group can undergo various reactions, such as poly-addition or hydrolytic ring cleavage. Both possibilities have already been used in the fabrication of contact lenses and scratch-resistant coating. Therefore, the hydrolysis and condensation reactions of the trialkoxysilyl moiety in GPTMS have been already studied. The mixture of GPTMS/3-aminopropyltriethoxysilane (APTS) was investigated in one and two step synthesis processes compared in the acid catalyzed sol-gel reaction in the mixed binder system. The two step process

provided clear sol while the one step process resulted in a milky suspension [12-13].

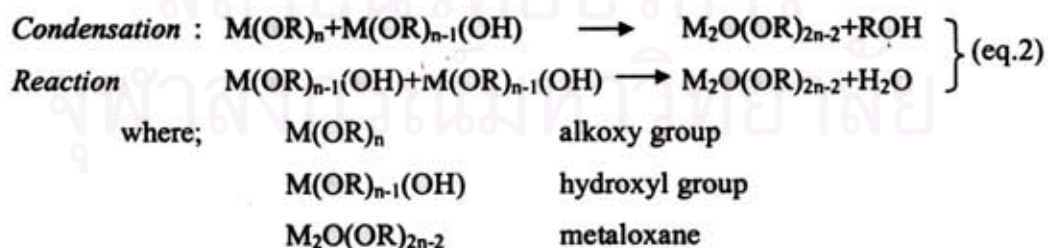
Sol-gel process

The sol-gel process was first initiated in the late 1800s [14]. The important stage refers to a low temperature method using chemical precursors that can produce glasses and ceramics with better purity and homogeneity than the high temperature conventional process. The process is used in various forms, such as monoliths, composites, including powders, fiber, coating, and thin films.

The sol-gel process is a chemical synthesis involving 2 main steps, viz. sol-gel transition and heat-treatment. The first step is a device for hydrolyzing metal alkoxides to obtain solution or sol (Eq.1), such solution or sol composes of an oxide skeleton and a solvent phase in the pores.



After the hydrolysis reaction, the product will be formed as gel through the condensation reaction (Eq.2). The gel transformation occurs due to more participation of water into the metal alkoxide molecule, consequently, inducing the condensation reaction. Eventually, hydrolyzed units become larger units with metal-oxygen-metal bridging.



The advantages of the sol-gel process are as follows [15]:-

- The thermal degradation of any materials is minimized with higher purity and stoichiometry since the temperature required in the process is low.
- It is easily to achieve a homogeneous control due to the fact that organometallic precursors containing different metals are frequently miscible.
- It is likely to obtain highly porous and nanocrystalline materials.
- There is no need for machine or melting in casting ceramic materials or producing thin films or fibers or monoliths because of easily applicable precursors.
- High degree in thickness uniformity over large areas results in the notably magnificent optical quality of materials leading to applications for optical components.
- It allows the production of amorphous materials via the low temperature of sol-gel process, which is basically below the crystallization temperature for oxide materials.

However, it should be noted that there are also some limitations from the sol-gel process. Those are [15]:-

- The precursors are often expensive and sensitive to moisture. The sol-gel process is time consuming, particularly where careful aging and drying are required.
- It is likely to encounter the problem of dimensional change, such as densification, stress cracking or cracking on drying.
- It is difficult to study the structures and properties of metal alkoxides, because they are too sensitive to moistures.

Surface Improvement via the Sol-gel Process

Almost hard coat liquids consist of inorganic (filler)/organic (reactant that is a solvent, catalyst, and other hydrocarbon compounds) to form hybrid network material. Therefore, it is not easy to maintain the best condition of the solution containing many reacting organic-inorganic compounds. Thus, it is

very important to maintain the temperature to retard the organic-inorganic reaction in the solution, which results in an increase in viscosity, causing it hard to coat on the lens. Then the xerogel film can be made using a dipping machine, the film thickness can be controlled by adjusting drawing and dipping speeds, and analyzed by UV-spectrometer. After coating lens, heat treatment is needed to make a dense gel film. This is a crucial point to obtain better film thickness and other optical properties; for example, if one uses a higher temperature, the lens would crack or striation due to collapse of the gel network.

In general, the coating process in a lens coating company uses the dipping method. The sol-gel method is easy to understand and proceeds in two steps, coating with dipping process followed by drying using thermal oven [15].

Hard Coat Process

Dipping Process (see Figure 1.1) is the process that the lenses simultaneously receive a layer of varnish on each surface. The lenses are cleaned using ultrasonic activated chemistry, then immersed in the liquid varnish bath from which they are removed at a constant rate to control thickness of the final coating, which is likewise dependent on viscosity of the liquid. The varnish is then polymerized by baking at a temperature of about 100°F/200°F. It then turns into a hard, solid film which endows the coated lens with resistance to scratching, its performance being a function of composition and thickness. All these operations are performed in controlled atmospheric conditions (clean room), with monitored temperature and humidity.

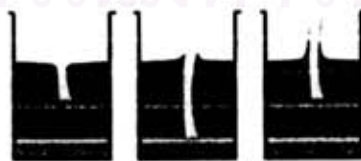


Figure 1.1 Principle of varnishing by dip coating.

Spinning process (Figure 1.2) is simple, and its principle makes it particularly suitable for small items which rotate symmetrically: the lens is attached to a rotary support at a controllable speed; a drop of the liquid varnish to be spread is applied to the lens centre. Rotation speed is accelerated until a uniform film covering is obtained by centrifugation. This method is readily adaptable to the manufacturing of small series of lenses; since the actual varnishing operation is performed very fast, it can be used to apply less stable, more complex varnishes than the dip coating procedure. Moreover, because of its simplicity and speed, it is used to varnish concave surfaces in US surfacing laboratories (where polymerization is often achieved in a few minutes' exposure to ultraviolet radiation). On the other hand, the resulting coatings often show poor abrasion resistance.



Figure 1.2 Principle of varnishing by spin coating.

The coating of titanium glycolate, zirconium glycolate and silatrane precursors on lens surface has been studied in this thesis. They are synthesized via the Oxide One Pot Synthesis (OOPS) process [11-12, 14]. These precursors are inexpensive and the synthetic reaction is simple and straightforward. Epoxy functionalized alkoxy silanes of GPTMS were used as surface modifiers for silica, titania, and zirconia particles to achieve water dispersible nanoparticulate coating materials. 3-APS was suggested in the system that may interact with a polyurethane substrate through hydrogen bonding between amino proton in 3-APS and carbonyl groups in the substrate [16]. The effect of sol-gel process parameters, which are the composition of sol-state solution,

such as ratio between metal alkoxide precursors and organic solvent, the cross-linker as an inorganic filler, coating condition focused on setting time (dipping time and drawing time) or coating speed and the curing temperature was studied.

Metal Alkoxide Precursors

Ksapabutr *et al.* (2003) [17] prepared zirconium and cerium glycolate complexes directly from the reaction of zirconium dioxide and cerium dioxide, respectively, with ethylene glycol. They were successfully synthesized with high yields, approximately 90%, and can be starting materials for further applications. All these metal alkoxides were prepared via the Oxide One Pot Synthesis (OOPS) process, which was a low cost and facile route. More importantly, they are moisture stable and inexpensive as compared to the commercial ones.

Phonthammachai *et al.* (2002) [14] prepared titanium glycolate using low cost starting materials, titanium dioxide and ethylene glycol, and triethylenetetramine as catalyst. The final product shows good moisture stability. Characterization of this product using XRD confirms that the product stability showed transformation from anatase to rutile phase up to 900°C.

Charoenpinijkarn *et al.* (2000) [13] prepared silatrane complexes by direct reaction of SiO₂ and trialkanolamines, and observed their potential as ceramic precursors via the hydrolytic sol-gel process method. The gelation behavior of silatranes was based on triisopropanolamine at different hydrolysis condition. The surface area and morphology of polarized ceramic products were found homogeneous microporous structures with high surface area (313-417 m²/g), depending on the process conditions. For example, the condition at 800°C of glass formed under more ionic conditions (MgO/H₂O) has the smallest pores and the largest surface area (417 m²/g).

Coating Materials

Man S.L. and Nam J.J. (2002) [18] synthesized organic-inorganic hybrid composites by the sol-gel method for hard coating agent of transparent

plastic. They used methyltriethoxysilane (MTES) and colloidal silica as starting materials. Coatings were prepared from suspensions containing colloidal silica and various amounts of MTES. Light transmittance of coating films increased over 2% compared with uncoated PMMA sheet. It was originated from decrease of the refractive index and the surface roughness. Surface roughness decreased by the increase of MTES content. Abrasion resistance of PMMA sheet coated with silica coatings increased with the addition of MTES and the optimum amount of MTES was 100 wt% to colloidal silica. The MTES adsorbed on the silica surface and formed a strong siloxane bonding between particles by the condensation reaction. The addition of curing catalyst, tetramethylammonium formate was found to be very effective to enhance the adhesion strength of coating agent to the substrates and reduce curing time.

Li *et al.* (2000) [19] developed transparent abrasion-resistant coating by the sol-gel reaction of alcoholic solution mixture of triethoxysilylated diethylenetriamine (f-DETA) and tetramethoxysilane (TMOS). The pot life of these coatings could be controlled from several min up to 20 h using acids of different acidity strength. These hybrid coatings were applied on substrates of bisphenol-A polycarbonate (bis-A PC), APEC HT9353[®] (a copolycarbonate manufactured by Bayer), brass and stainless steel utilized to demonstrate the effectiveness of the coating. Using f-DETA/TMOS coating if the adhesion between the coating and the substrate is sufficiently strong, principally it can protect polycarbonates, other polymeric and metallic substrates. The scanned images of Taber wear tracks on both coated and uncoated copper substrates showed that for the uncoated control sample, a clear wear track was seen after only 10 cycles of abrasion. The samples protected by f-DETA30TMOS30W5-HCl27 coating displayed little evidence of a wear track after 250 and 500 cycles of abrasion. It is also worth indicating that the coated copper substrates maintained the original reddish brown color even after heating at 170°C for 4 h. The f-DETA30TMOS30W5-HCl27 coating to brass, an alloy of copper, is also effective in protection, exhibiting little visible wear after 100 and 200 cycles of abrasion. For stainless steel the poorer performance of the sol-gel coating on

steel substrate is due to the lower level of adhesion between the substrate and the f-DETA/TMOS coating. It is very likely for these sol-gel derived coatings to be used as general abrasion resistant coatings for plastic and soft metallic substrate.

Urreaga J.M. *et al.* (2000) [20] studied the abrasion in the tumble test of PC sheet coated with different acrylic hybrid materials, viz. TEOS, 3-methacryloxypropyl-trimethoxysilane (MPS) and methylmethacrylate (MMA). The coated substrates were cured at 120° and 140°C for different times. It was found that the lower degree of polymerization could explain the lower abrasion resistance of coatings cured at 120°C for 4 h. However, the polymerization was almost complete after curing these acrylic coatings for 8 h. The poor abrasion resistance of samples cured at 120°C for 24 h, or at 140°C for 8 h, may be assigned to the over curing of the coatings. Similar results were found in the infrared analysis of the curing of MMA-containing coatings. The infrared analysis of the curing processes showed that in order to achieve the highest abrasion resistance, these acrylic hybrid coatings must be fully polymerized, but over curing must be carefully avoided. Finally, a linear correlation was found between the abrasion resistance of these coated samples (as measured by the Tumble test) and their micro-hardness.

Havey *et al.* (1999) [21] improved the stability of invention related to coating compositions when applied on the polymeric substrates where it is highly desirable to provide substrates with abrasion resistant surfaces, and cured to provide transparent. The coating compositions were influenced by a variety of factors, including solvent system, pH, concentration and ionic strength in a variety of different ways. In some instances, the colloidal silica is desirable to be added in last step of reaction sequences. In other instance, it was added in the first step of reaction sequences. Likewise, it is possible to add other metal oxides into the coating compositions of the present invention. Metal oxides can be added to the inventive coating to provide specific properties of the cured coating, such as abrasion resistance, refractive index, anti-static, anti-reflectance, etc. Examples of other metal oxides, which are used

in the coating compositions, are zirconia, titania, ceria, tin oxide, and their mixtures.

Chenghong L. and Garth L.W. (1998) [2] observed a chemical bonding mechanism based on aminolysis of the carbonate groups by 3-APS. The 3-APS primer and the aminolysis mechanism may also be extended to PMMA substrate, an excellent glazing material. Similar to bis-A PC, this polymer can also be treated with the sol-gel coating to increase abrasion resistance. On this occasion, however, 3-APS reacted with the ester groups and became linked to the substrate through amide groups. Dispersion IR or XPS analyses also revealed that aminolysis occurred at the surfaces of bis-A PC, CR-39 resin and PMMA when in contact with a solution of 3-APS in IPA. The results also showed that under similar conditions, CR-39 resin was less swellable and the aminolysis at its surface occurred to a lower extent. For that reason, a more concentrated 3-APS solution was required to obtain the same level of aminolysis. The treatment of bis-A PC or CR-39 with 3-APS primer allowed the formation of a thin 3-APS gel layer, which facilitated the covalent bonding of a layer of alkoxy silane-containing sol-gel coating on the modified polycarbonate substrate.

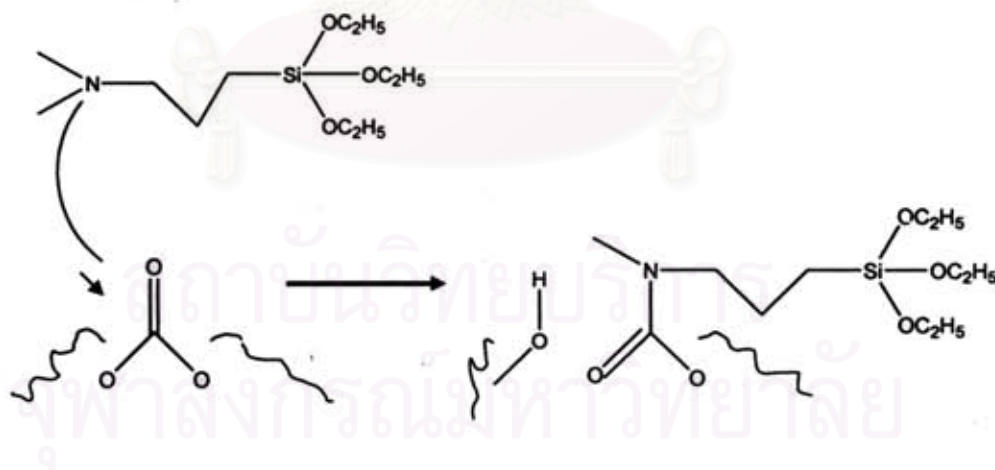


Figure 1.3 The covalent bonding of a layer of alkoxy silane-containing sol-gel coating on the modified polycarbonate substrate.

Wen *et al.* (1995) [5] prepared novel abrasion resistance coating materials by sol-gel method and applied on the polymeric substrates, bisphenol A polycarbonate and diallyl diglycol carbonate resin (CR-39). These coatings were inorganic/organic hybrid materials synthesized from 3-isocyanato-propyl triethoxysilane functionalized organics and metal alkoxide. The substrates were spin coated onto their sheet and thermally cured to obtain a transparent coating of a few microns in thickness. The study was found greatly improved by treating the polymeric substrates with a primer solution of isopropyl alcohol (IPA) containing 3-aminopropyltriethoxysilane (3-APS). Testing showed strong hydrogen bonding between ester group in polycarbonate substrate and amino group of 3-APS.

Hydrophilic Coating Solution

Ki C.S. *et al.* (2003) [22] synthesized inorganic-organic hybrid coating solutions with both long-term hydrophilic and crack-free properties by mixing a silane coupling agent, glycidoxypropyltrimethoxysilane (GPTMS) and colloidal silica suspension through the sol-gel route. They investigated the effect of pH in colloidal silica suspensions on chemical structure of coating solutions that coated on polyethyleneterephthalate (PET) film substrates. The pH of colloidal silica suspensions adjusted before adding the GPTMS had a profound effect on chemical structure of the coating solutions and hydrophilic property of the coating films. $^{29}\text{Si-NMR}$ spectroscopic studies showed that the solution prepared under an acid condition (pH4) consisted of hydrolyzed GPTMS monomers without siloxane bond and dimer with one siloxane bond, whereas a basic condition (pH9.6) was made up larger oligomers with two or three siloxane bonds. Especially, in the case of coating films prepared under highly acidic conditions (pH1 and 2), the contact angles were less than 5° , which was super-hydrophilic.

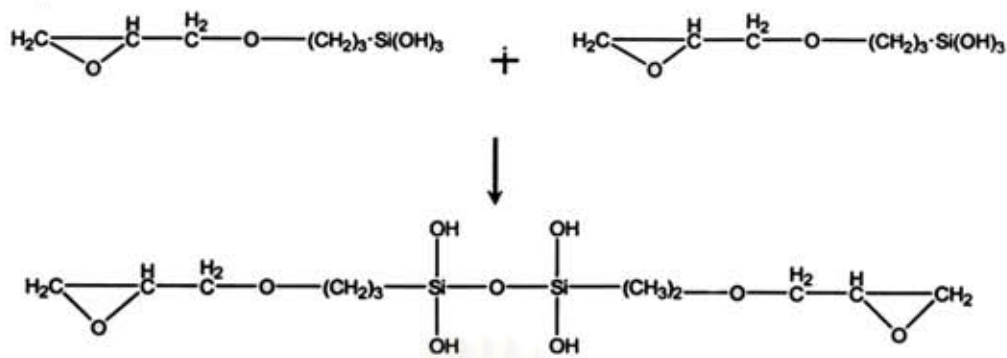


Figure 1.4 Condensation of silanols in hydrolyzed GPTMS monomers to produce dimer and larger.

Dan Y. *et al* (2003) [10] studied water-based polymer coating materials used for the surface energies by the complexation of two component polymer lattices containing polydimethylsiloxane (PDMS) and having chemically complementary structures. The film-forming performance of the polymer lattices, the surface structures and properties of the coatings formed by the polymer lattices were studied by means of scanning electron microscopy and by the measurement of mechanical strength, thermal performance, water absorbability, and contact angle. When the two-component polymer lattices [the poly(methyl methacrylate-co-butyl acrylate-co-methyl acrylic acid)/polydimethylsiloxane system (PA latex) and the poly(methyl methacrylate-co-butyl acrylate-co-pyrrolidone)/polydimethyl-siloxane system (PB latex)] were compared, the complex polymer latex formed by the complexation of the PA latex with the PB latex had the best film-forming performance, with more smooth and less cracks coatings, and also had a unique structure, a higher mechanical strength and elongation, a higher decomposing temperature and better water resistance.

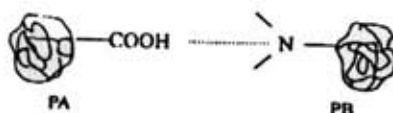


Figure 1.5 Schematic diagram of the interparticle interaction through the hydrogen bonding of the $-\text{COOH}$ group in PA with the $-\text{N}-$ group in PB.

Kim D.H. *et al.* (2003) [12] prepared APTS binder, maintaining clear sol and used as reactant for mixed binder, GPTMS/APTS, in acidic condition. The study was investigated in one and two-step synthesis processes. The one step process was the simultaneous addition of GPTS, APTS and water with the ratio of 20:5:12. The other was a sequential addition of pre-made GPTS binder and APTS binder. In case of the one step process, when the mole ratio of GPTS to APTS decreased from 16 to 4, about 36% of epoxy ring appeared to be opened by amino group of amino group of APTS. On the other hand, for the two-step process, only 8.7% of epoxy ring was opened by amino group of APTS. This might be explained by the slower hardening in the two-step prepared mixed binder system, because it was not easy to attack the epoxy group of pre-made polymerized GPTS. Using the two-step made clear sol, while the one step process resulted in a milky suspension.

Steven R.D. *et al* (2003) [23] prepared a number of epoxy-silica hybrid materials by sol-gel/amine curing reaction of GPTMS for use in coating on steel. The precursor molecule possessed both epoxy and silicon alkoxide functionality and interlinked inorganic-organic networks was formed. GPTMS can undergo a variety of reactions during the preparation of a hybrid by a sol-gel route. Pre-hydrolysis of GPTMS with a stoichiometric amount of acidified water left the epoxy groups intact. Diethylenetriamine (DETA) was used to open the epoxy rings and form the organic network to an extent determined by initial ratio of amine to epoxy groups. Thus, increasing the concentration of DETA increased the organic network formation. The inorganic networks consisted mainly of T^3 -siloxane units and were substantially formed at room

temperature. Curing at 150°C helped formation of both networks. Use of a low DETA concentration results in an incomplete organic network at room temperature and there is sufficient freedom for the inorganic network to form. Low DETA formations, therefore, required thermal curing (or additional catalysts) to complete and highly cross-linked organic network that constrained and inhibited formation of the inorganic network.

Winkler R-P *et al.* (1999) [11] used epoxy functionalized alkoxysilanes as surface modifiers for alumina, silica or zirconia particles to achieve water dispersible nanoparticulate coating materials. They found that when an amino functionalized alkoxysilane could be used as condensation catalyst and the nano-composite material was thermally cured at 130°C after flow or spray coating on penetrated polycarbonate substrates. The coating showed excellent adhesion proved by cross cut and tape test. After 1000 cycles Taber abrasion test (CS-10F, 500g, DIN 52347) losses of transmittance due to scattering of 2-6% were achieved with a coating thickness of about 5 µm. The transparent hard coatings showed an abrasion resistance comparable to solvent-based systems. This technique could set up new fields for sol gel materials, especially in large area applications.

Yunfa C. *et al.* (1998) [24] prepared organic-inorganic nanocomposite protective coatings on aluminum substrates using spinning technique with the concept of incorporating homogeneously nanosized particles (of AlOOH, Al₂O₃, ZrO₂, SiC) into molecular organic-inorganic hybrid matrices. The hybrid matrices were derived from epoxysilane and bis-phenol A with imidazol as catalyst. The AlOOH particles were derived from aluminum isopropoxide and introduced into the hybrid sols directly, and Al₂O₃, ZrO₂, SiC particles were first surface-modified with Si-OH from hydrolyzed TEOS. In coating by spinning method, only a small quantity of sol was normally needed, leading the hot sol to cool down quickly. The result showed nothing that the performance of coatings derived from the sol kept at room temperature was even better than those from the sol kept at room temperature was even better then those from the sol at 60°C. The endothermic peak accompanied by weight loss was attributed to the removal of residual water and solvent. An exotherm at about 150°C

appeared to be the result of decomposition. If the coating was heated to 150°C, it became yellow. From the IR spectra, it was found that the Si-OH in the coating disappeared at 150°C. So the curing temperature in this system was normally fixed at 130°C. The surface characteristics of the coatings were observed using SEM and the particle size on the SEM micrographs was slightly larger than that in the raw materials. In this system, the introduction of bisphenol A and boehmite sol should improve the coatings that are dense, smooth and flexible, and inhibited corrosion.

Daniels M.W. and Francis L.F. (1998) [25] investigated the adsorption of GPS onto silica colloids (20 nm diameter) suspended in an IPA/water solution. Coating microstructures consisted of packed colloids with varying amounts of a GPS siloxane polymer on colloid surface and filling in porosity. When the amount of GPS added just surpassed that needed to fill the pores (up to $R=0.5$); the better performance was due to the decrease in porosity and the improved bonding between particles. Drying at higher temperatures improved abrasion resistance, showing the added benefits from chemically cross-linking the siloxane and improved bonding between siloxane and particles. The critical cracking thickness of the coatings increased dramatically when the amount of silane added was sufficient to fill the pore space. Hardness and abrasion resistance of the coatings improved with GPS content, but deteriorated when the GPS content was far in excess of that needed to fill the pores.

Objectives

The objectives of this research work are:

- To coat zirconia, titania and silica on ophthalmic lens via the sol-gel method using zirconium/titanium glycolate and silatrane, respectively, as precursors.
- To study parameters affecting the sol-gel process of the precursor coated on the lens surface.
- To evaluate the scratch resistance property of coating films on ophthalmic lens.

- To compare refractive index of each precursor coated on the ophthalmic lens.



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Chapter II

Experimental

All glassware was cleaned by soaking in a sodium hydroxide cleaning solution bath, followed by washing, rinsing with water and then drying in an oven at 60°C prior to use.

Materials

Titanium dioxide (TiO_2) having surface area of $12.2 \text{ m}^2/\text{g}$, fume silica with surface area of $280 \text{ m}^2/\text{g}$, average particle size of $0.007 \mu\text{m}$, and zirconium hydroxide were purchased from Sigma-Aldrich Chemical. They were used as starting materials and kept in a dry environment prior to use to prevent moisture adsorption. Ethylene glycol (EG) was purchased from J.T.Baker Company Co., Ltd., and used as reaction starting material and solvent. Commercial grade triethylenetetramine (TETA) was purchased from Facai Polytech Co., Ltd., used as catalytic base and used as received. Acetonitrile was purchased from Lab-Scan Company Co., Ltd., used as received. Triethanolamine (TEA), was supplied by Carlo Erba reagent and used as received. Sodium hydroxide was purchased from Merck Company Co., Ltd. (Germany) and used as received. Methanol was purchased from Scharlau. Hydrochloric acid, used as acid catalyst, was purchased from BDH Laboratory Supplies and used as received. Isopropanol and ethanol were purchased from Lab-Scan and used as received. 3-Aminopropyltriethoxy silane (3-APS) was purchased from Fluka chemical and used as a primer. 3-Glycidoxypropyl-trimethoxysilane (GPTS) was purchased from Aldrich Chemical Co. Inc. (USA), and used as an organo silane coupling agent. Polyurethane polymeric substrate: sheet $1.5 \times 1.5 \text{ cm}^2$, $1.5 \times 5.5 \text{ cm}^2$, plano-ophthalmic lens diameter 5.5 cm. was supported from Thai Polymer Lens Co., Ltd.)

Equipment

Thermogravimetric analysis was carried out on a Du Pont instrument, Du Pont TGA2950, using a flow rate of 25°C/min, a heating rate of 10°C/min and a temperature range from room temperature to 750°C. FTIR spectra was analyzed on a Bruker instrument, model EQUINOX55, using samples mixed with dried KBr to obtain sample pellets. The scanning electron micrographs were characterized using Joel SEM-JSM5200 to observe the abraded surface of coating. Mass spectra were obtained using FISIONS Instrument (707 VG Auto spec-ultima mass spectrometer, Manchester, England) with a VG data system, employing a direct probe inlet and using the Cs gun to ionize sample mixed with glycerol matrix. The mass range of sample was set from $m/z = 20$ to 1500. UV-visible spectrophotometer (UV-2401/2501 PC) was used to measure light transmission of abraded coated substrate, using a wavelength range of 400 to 700 nm in correlated haze mode. Abbe refractometer type 3T was used for liquid and solid refractive index measurement. The scale was engraved with refractive indices based on sodium D rays at 20°C. The wavelength of D rays was 589.3 nm. The scale's range was 1.3000~1.7100 with the smallest calibration of 0.0002; the smallest possible eye measurement reading, 0.00005; and ± 0.0001 measurement precision. BET surface area and nitrogen adsorption characterization were performed using an Autosorb-1 gas sorption system (Quantasorb JR.). Test materials were outgassed at 170°C under the reduced pressure, prior to analyses. Powder X-ray diffraction patterns were examined using a RIGAKU RINT 2000 connected with $\text{CuK}\alpha$ source of radiation and operated at 40 kV, 30 mA with Ni filter.

Methodology

Zirconium Glycolate Precursor Preparation

Zirconium alkoxide was synthesized via the Oxide One Pot Synthesis (OOPS) process. 10 mmol of zirconium hydroxide was added into a two neck round bottom flasks containing 20 mmol (0.80 g.) sodium hydroxide and 35 ml of ethylene glycol (EG). The mixture was stirred to obtain homogeneous solution and heated at the boiling point of ethylene glycol (200°C) in a silicone oil bath for 12 h under nitrogen atmosphere to remove water (by-product)

generated from the reaction. The reaction mixture was continued till clear solution was obtained, meaning complete reaction. The clear solution was then cooled under nitrogen atmosphere for overnight. The white solid was precipitated after the addition of 2-5% of dried methanol in acetonitrile, followed by washing with acetonitrile until the filtrate had no color. The powder product was then dried under vacuum (0.1 mmHg) at room temperature. The solid product was characterized using FTIR, TGA, and FAB⁺-MS [17].

Titanium Glycolate Precursor Preparation

A mixture was prepared from 0.025 mol (2 g.) titanium dioxide (TiO₂) with 0.0074 mol (3.65 g.) triethylenetetramine (TETA), used as a catalyst, and 25 ml of ethylene glycol (EG), as a solvent. The mixture was heated to 200°C for 24 h and then centrifuged to separate the unreacted TiO₂ from the solution part. The excesses EG and TETA were removed by vacuum distillation to obtain the crude product. The white solid product was then washed with acetonitrile and dried in a vacuum desiccator. This solid was characterized using FTIR, TGA, and FAB⁺-MS [14].

Silatrane Precursor Preparation

A mixture was prepared by mixing the fumed silica with triethanolamine (TEA), as a catalyst, in the ethylene glycol (EG), as a solvent at the following ratio: 0.10 mol fume silica, 0.125 mol TEA and 100 ml of ethylene glycol. The important step of this reaction was to heat the mixture at the boiling point of ethylene glycol under nitrogen atmosphere to remove water as by-product along with EG. The white solid product was obtained after the reaction was complete, cooled to room temperature, precipitated out and finally washed with dried acetonitrile. The product was characterized using FTIR, TGA, DSC, and FAB⁺-MS [13].

Sol-gel Process of Precursors

Zirconium Glycolate

The sol-gel process was carried out at 25°C. Sodium glycozirconate was first dissolved in water using the H₂O/alkoxide molar ratio of 24. The separated gel was

oven dried at 80°C for 12 h and then calcined at 800°C for 2 h. The zirconia powder was characterized using BET and SEM [26].

Titanium Glycolate

The hydrolysis of titanium glycolate (0.026 g) was carried out by addition of 160 μL of 1M HCl and distilled water mixture with the volume ratios of 35:125. The mixtures were magnetically stirred and heated in a water bath at 50°C until the clear gel occurred. The gel was calcined for 2 h at 800°C. The titania powder was characterized using BET and SEM [27].

Silatrane

Silatrane product was dissolved in the hydrolysis solvent (0.01M HCl) at a concentration of 150% w/v. The solution was stirred until homogeneous and heated in a 40°C water bath until the solution was viscous to form gel. The gel was then calcined at 800°C for 2 h. The silica powder was characterized using BET and SEM [13].

Preparation of Hard Coat Solution via Sol-gel Process

Partially hydrolyzed metal alkoxide was prepared by dissolving the material precursor, viz. zirconium glycolate, titanium glycolate and silatrane, in acid catalyst solution of 1M HCl in isopropanol. The addition of GPTS coupling agents to the suspension sol was needed to avoid the problem of cracking at high temperature. The hydrolysis and condensation reactions were pH dependent. The solution was mixed for approximately 5 h followed by adjusting pH in the solution so as to control the size of molecule during condensation reaction [25]. The conditions used in this part were summarized in table 2.1.

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Table 2.1 Coating material conditions

Hard Coating Mixture	Type of Precursors		
	Titanium glycolate	Silatrane	Zirconium Glycolate
Precursor(g)	0,0.1,0.05	0,0.1,0.05	0,0.1,0.05
1M HCl (μL)	0,100,300,700,1000	0,100,300,700,1000	0,100,300,700,1000
IPA (μL)	0,100,300,700,1000	0,100,300,700,1000	0,100,300,700,1000
GPTS (μL)	0,300,600,1000	0,300,600,1000	0,300,600,1000
3-APS(%Tot.Vol.)	0,3,4,5,10	0,3,4,5,10	0,3,4,5,10

Dipping Process

The plano lenses (casting from hi-index co-monomer of polyurethane material) were chemically etched using the condition of 5-10%wt KOH for 5-10 min at the temperature of 20°-60°C in the ultrasonic bath. These lenses were washed using de-ionized water twice and dried in oven at approximately 90°C to evaporate residual water. The etched lens was dipped in the bath containing the prepared organometallic precursor solution. For the dip-coating process the pull-up speed needed to be controlled to maintain the thickness between 1.6-2.0 μm. The crosslinking process on the hard coat lens was set at 60°-70°C (for pre-curing) for 10-20 min, and 110°-150°C for 2.5 h (for post curing). The coated materials were characterized using FTIR to determine its functional groups, SEM to determine coating microstructure and UV spectrometer to determine surface damage.

Testing

Adhesion Property Test by "Direct Method"

The direct method is used to provide a quantitative index of the thermal cured coating on the substrate. The technique was based on the first forming and adhesive bonding with the coating material. Force was applied to determine a value for practical adhesion. The force required to pull the film off the substrate was F. The stress of adhesion was σ . The unit area was A where A was 0.5 cm² in this study.

$$\sigma = F/A \quad (\text{eq.2.1})$$

Abrasion Resistance Test by Steel Wool Abrasion

This test was performed using #000 grade steel wool. The steel wool was rubbed across the lens surface with 1.0 Kg (2.2 lbs) force continuously applied for 10 cycles. This rubbing can be done using an oscillating machine or by hand. The surfaces are graded as “pass” if the scratching is less than 40. Observation result of coated lens was compared with uncoated one and the surface was measured degree of abrasion using SEM.

Refractive Index Test

The refractive index of lenses after coating must be above the value obtained from uncoated lens. Approximately, the values are between $n_e = 1.591-1.599$ and $n_d = 1.596-1.595$ (where n_e is the index for $\lambda_e = 546.07$ nm at green Hg and n_d is the index for $\lambda_d = 587.56$ nm at yellow He). The value can be obtained using refractometer.

Durability Test in Boiling Water

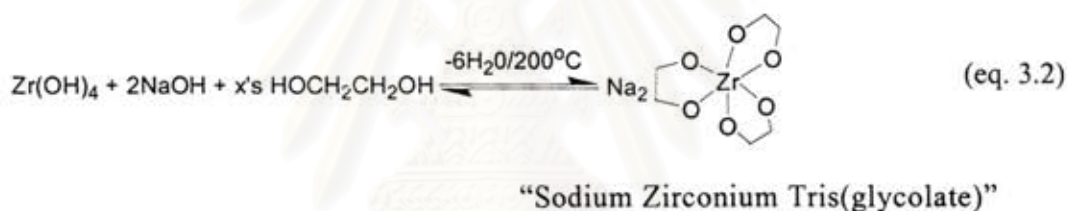
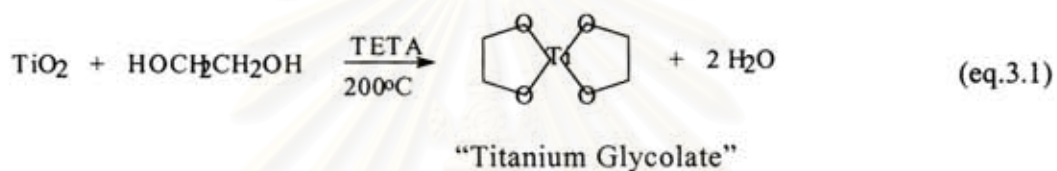
Durability testing technique includes repeated immersion in boiling water (deionized or added dissolved solids), cyclic humidity exposure, dry heat exposure and solvent attack. Comparison of the result between different materials was measured by % transmission value of UV-VIS spectrophotometer.

Chapter III

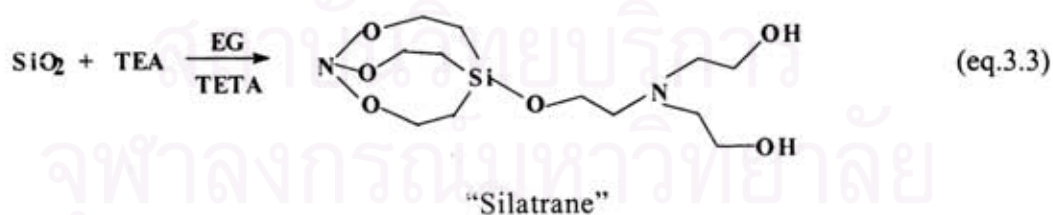
Results and Discussion

Synthesis of Titanium/Zirconium Glycolates and Silatrane Precursors

Titanium and zirconium glycolate precursors were synthesized via the Oxide One Pot Synthesis (OOPS) process using inexpensive and widely available TiO_2 as starting material, ethylene glycol and triethylenetetramine (TETA), as a base. Since water is a by-product of the reaction, it must be removed from the system to push the reaction forward, as shown in eq.3.1-3.2.



Like-wise, silatrane precursor was synthesized via the One Pot Synthesis (OOPS) process using inexpensive and widely available SiO_2 to react with TEA, ethylene glycol as solvent and TETA as catalyst. The reaction is given in eq. 3.3.



Characterization of Precursors

Thermogravimetric Analysis (TGA)

The TGA thermograms of precursors were analyzed in a nitrogen atmosphere, as shown in Fig. 3.1. In the case of silatrane, the organic ligands decomposed at around 310°-420°C and the final ceramic yield, 18.40%, was close to theoretical ceramic yield, 18.66%. The titanium glycolate precursor showed the weight loss around 310°-350°C corresponding to the decomposition of organic ligand and remaining organic residue. The final ceramic yield was 46.80% as compared to 47.56% for the theoretical ceramic yield based on a final ceramic product TiO₂. The TGA curve of zirconium glycolate shows the major thermal decomposition of organic ligand at 350°-545°C.

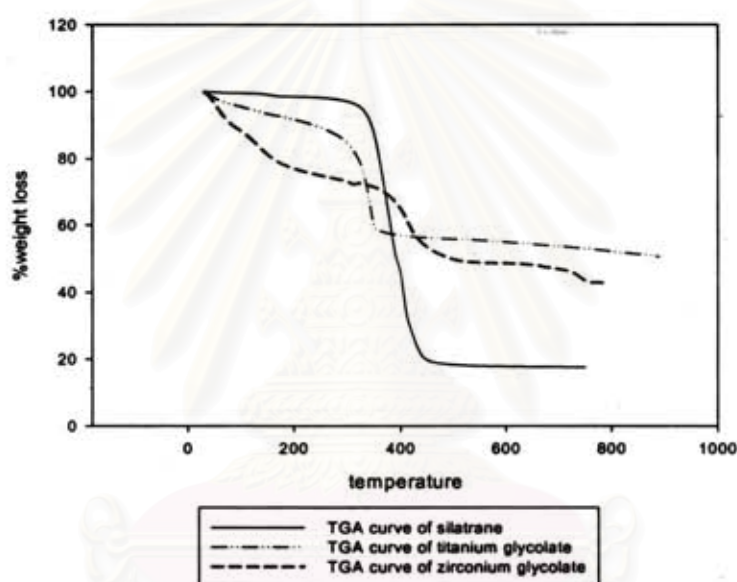


Figure 3.1 TGA profiles of precursors.

Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 3.2 shows the FTIR spectra of silatrane, titanium glycolate and zirconium glycolate, respectively. The results indicate the functional groups of metal alkoxide of these 3 precursors in the region of 1090-1015 cm⁻¹ for Si-O-Si [13], three bands at 1130, 1080, and 1042 cm⁻¹ can be assigned to C-O-Ti [14] and 1090 cm⁻¹ for Zr-O-C [26].

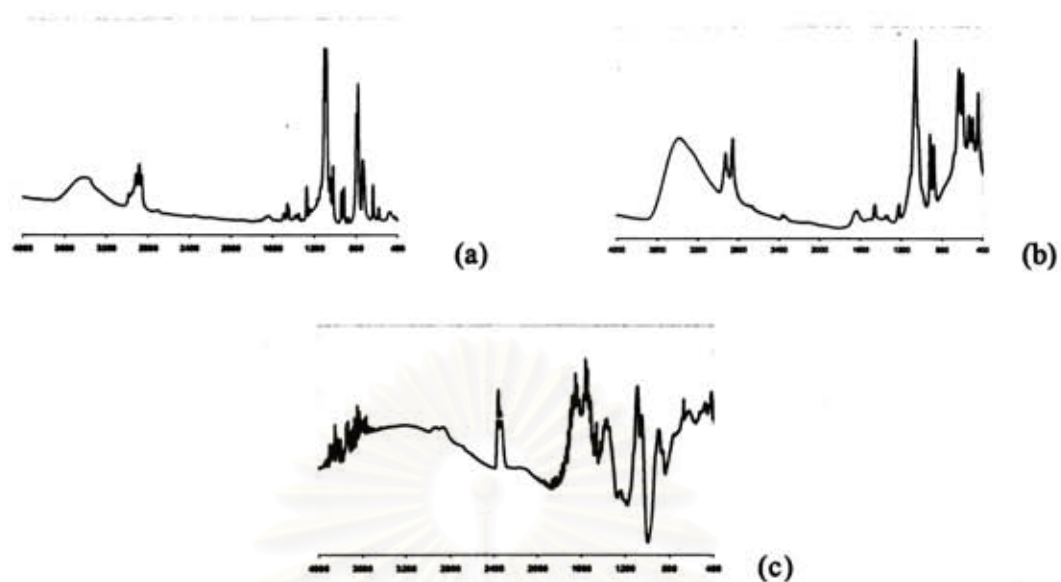


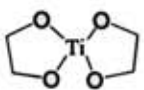
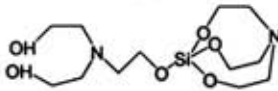
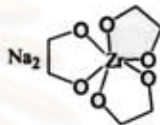
Figure 3.2 FT-IR spectra of a) silatrane, b) titanium glycolate and c) zirconium glycolate.

FAB⁺-MS spectroscopy

Mass spectral analysis of the precursors is summarized in Table 3.1. Indication of the molecular ion at m/e 323 (36.4% intensity), m/e 169 (8.5% intensity) and m/e 182 (100% intensity) identifies the product structures of silatrane, titanium glycolate and zirconium glycolate, respectively.

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Table 3.1 FAB⁺-Mass spectrum results of precursors

m/e	%Intensity	Proposed Structure
169	8.5	 + H ⁺ Titanium glycolate
323	2.6	 + H ⁺ Silatrane
169	30.6	 + H ⁺ Zirconium glycolate

Characterization of Silica/Titania/Zirconia

The particle morphology of the samples calcined at the temperature of 800°C is shown in Fig. 3.3. A finely-divided morphologies of all products were formed. Silica giving a surface area of 415 m²/g shows the finest morphology while titania and zirconia are formed consisting of spherical particles approximately 1 μm in size with surface area around 125 and 130 m²/g, respectively.

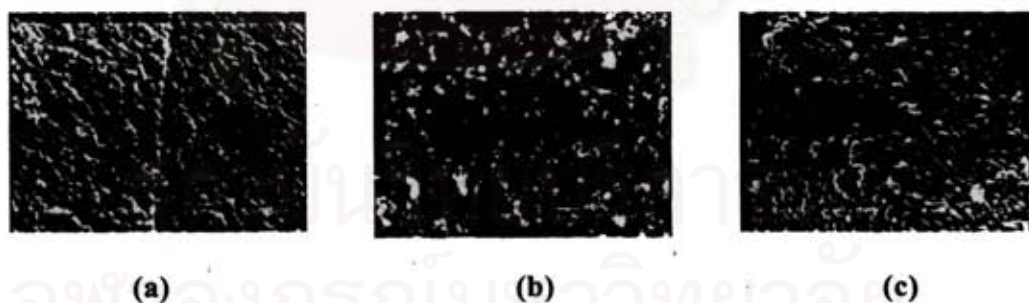


Figure 3.3 SEM micrographs of (a) silica, (b) titania and (c) zirconia

Synthesis of Hard Coating Materials in Sol-State

Hard abrasion-resistant coatings for ophthalmic plastics were obtained from mixing each precursor with 1M HCl, isopropyl alcohol, 3-glycidoxypropyl-

trimethoxysilane (GPTS) used as an organosilane coupling agent and 3-aminopropyltriethoxysilane (3-APS). The silatrane hard coating solution was clearer than titanium and zirconium glycolate solutions. The solution viscosities of those three precursors were higher, indicating that the hydrolysis and condensation reactions took place to form network.

Characterization of Hard Coating Materials

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical nature of the coatings was measured and followed the hydrolysis and condensation reactions in the sol-gel process using FTIR. The results showed the main chemical transformation during the sol-gel reaction, as shown in figure 3.4. FTIR spectra showed small bands at 1256, 643 and 613 cm^{-1} of a symmetric ring of epoxy and Si-O groups. The Si-O-C group in GPTS is easily recognized by strong band at 1090-1015 cm^{-1} . After the hydrolysis reaction occurred this peak became smaller and the peak intensities of Si-O(H) and (Si)O-H stretching at about 900 and 3400 cm^{-1} became bigger.

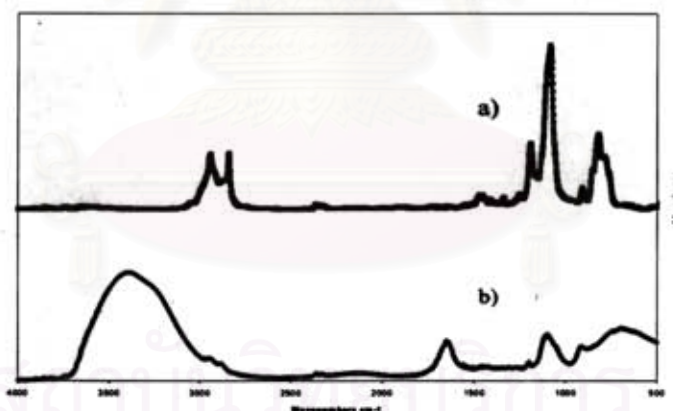


Figure 3.4 FTIR spectra of a) GPTS and b) the hydrolyzed GPTS.

Figure 3.5 shows the time dependence of the silatrane coating solution on the hydrolysis and condensation reactions. As the time increased to 2 h, figure 3.5a), the Si-OH peak was much larger, suggesting that the hydrolysis reaction occurred, giving Si-OH. After the time increased to 5 h and 15 h, figures 3.5b) and 3.5c), the Si-OH peak became much smaller probably due to

the fact that the condensation reaction overcame the hydrolysis reaction to result in the transformation of Si-OH to Si-O-Si peaks at 1090 cm^{-1} [13]. The hydrolysis and condensation seem to reach equilibrium after the time went up to 20 h.

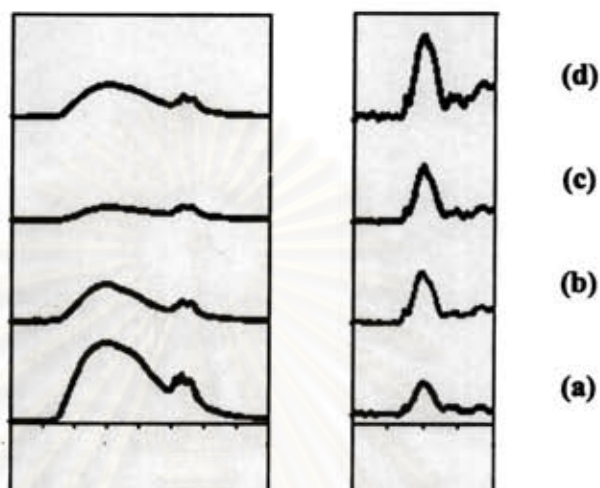


Figure 3.5 FTIR spectra of the time dependence of silatrane coating solution after a) 2, b) 5, c) 15 and d) 20 h reaction time.

The time dependence of the titanium coating solution shown in figure 3.6 indicated that the hydrolysis and condensation reactions seemed to be reversible between Ti-OH and Ti-O-Ti since the Ti-OH peak became larger at 15 and 20 h reaction times while the peak was much smaller at 2 and 5 h reaction times.

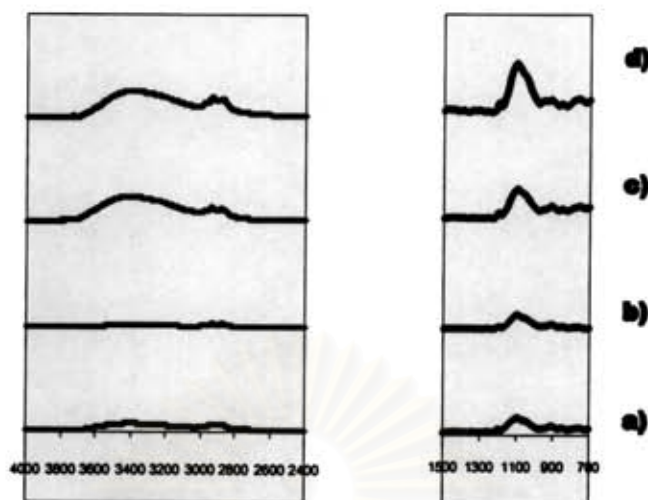


Figure 3.6 FTIR spectra of the time dependence of titanium glycolate coating solution after a) 2, b) 5, c) 15 and d) 20 h reaction time.

The time dependence of the zirconium coating solution on the sol-gel process is shown in figure 3.7. The results are similar to the titanium glycolate case. According to Lin et al. [18], the peak of Zr-O-Si should be increased with increasing reaction time at 1015 cm^{-1} [28], however, in this case, it is slightly increased. This is probably owing to the more moisture stability of our zirconium glycolate.

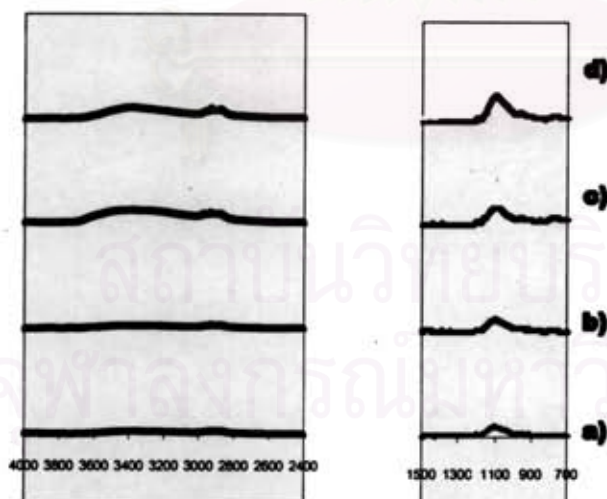


Figure 3.7 FTIR spectra of the time dependence of zirconium glycolate coating solution after a) 2, b) 5, c) 15 and d) 20 h reaction time.

The Formation of Coating Solution

The appearance results of coating solution at different concentration were compared with TS56DX coating solution used in industries for hi-index lens. It was found that the suitable quantity of precursor used for coating was found to be 0.05 g. At 0.1 g. of the precursor, the obtaining solution was precipitated. Amount of the curing agent, 3-APS, also affects the coating appearance. Too high 3-APS concentration as 5% created milky solution while too low concentration as 3% gave no reaction.

Addition of 1M HCl resulted in a clear solution because of its behavior as catalyst in the hydrolysis reaction of the sol-gel process. It converts the precursors to a new M-OH bond. However, the amount of 1MHCl affects the reaction rate. In this study, it was found that too much acid quantity, viz. 1000 μL , resulted in too fast hydrolysis and condensation rates, making the coating solution become gel too fast, while less than 300 μL of 1MHCl provided too slow reaction rate, giving milky coating solution.

Isopropyl alcohol was used to adjust the polarity difference between water and non-polar component as GPTS [22]. At the amount of IPA less than 700 μL , the coating solution became immiscible.

The quantity of coupling agent (GPTS) used as an organic binder in this work was 300, 600 and 1000 μL . Three methoxy groups and the epoxy group in GPTS were hydrolyzed and attacked by curing agent (3-APS), respectively, to form new strong bond in the coating solution and produce cross-linking structure on the film surface. Therefore, the case of coating solution prepared without GPTS showed the milky sol. The reason, as discussed by Song et al [29], is that the reaction between GPTS and hydrolyzed precursor is easier and faster, as compared to the reaction between 3-APS and hydrolyzed precursor, since the methoxy group (Si-OCH_3) in GPTS can be hydrolyzed faster with acid solution to form silanol groups (Si-OH) than the alkoxy group in 3-APS. Thus, immiscible solution occurred in the solution without GPTS. For all three precursors, they showed the same trend. Milky sol occurred in the case that either quantity of 1M HCl is less than 10% by total weight or there was no addition of GPTS.

The Formation of Coating Film

Table 3.2 shows the state of the coating films on polyurethane sheets in various concentrations of coating composition. The quantities of precursor and curing agent, 3-APS, were fixed at 0.05g ($\sim 1.468 \times 10^{-4}$ mol) and 4%, respectively. The results are compared with commercial coating solution, viz. TS56DX, which has no curing agent added. All concentrations were prepared as clear solution. However, different concentration gave different appearance on the coated surface. Using UV-visible spectroscopy the result of surface's appearance [Designation: D1003-00] shows that the higher %transmittance results in the clearer surface.

The case having no precursor was set as the reference, table 3.2a). The solution contained only 1M HCl, IPA, GPTS and 3-APS. The surface result was rather rough and looked like white or murky powder if the GPTS amount was lower than that of 1M HCl because of too much acid to generate a suitable sol-gel transition.

From table 3.2b), the addition of 0.05g precursor showed cracks free and transparent film. Transparent thin films without crack and haze are obtained in the 1M HCl:IPA:GPTS:%APS ratio of 700:1000:600:4%, 300:700:300:4%, 300:700:600:4% and 300:1000:300:4%. It should be noted that the film with good transparency and smooth surface could be obtained when the quantity of 1M HCl is not more than GPTS quantity and the ratio between HCl:IPA should not be lower than 1:1.4, as can be seen in the ratio of 300:700, 300:1000 or 700:1000 μ L. To obtain transparent and low haze thin film, the ratio HCl:GPTS has to be 1:1.

Both tables 3.2c) and 3.2d) show that smooth thin film of both coating compositions has a limit. As discussed previously, the quantity of GPTS must be more than 1M HCl to obtain a good transparency. In the case of zirconium glycolate, the condition that can improve the smoothness of the surface is to use the HCl:GPTS ratio of 1:1 to 1:2.

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Table 3.3a) References (the solutions containing only 1M HCl, IPA, GPTS and 4%tot.vol.3-APS)

Solution	Coating Composition			% Transmittance (λ, nm)			UV Cutoff	Appearance of Surface After Coated			
	Acid Catalyst HCl (μL)	Solvent IPA(μL)	Curing Agent GPTS (μL)	780	400	0	@%T=0	Smoothness	Roughness	Transparency	Murky
TS56DX	-	-	-	90.30	20.50	361.00	389.00	√		√	
Reference	700	700	300	63.82	13.64	361.00	390.00		√		√
Reference	700	700	600	83.59	19.20	363.00	390.00		√	√	
Reference	700	1000	300	56.27	12.76	364.00	390.00		√		√
Reference	700	1000	600	82.91	19.84	364.00	390.00		√	√	
Reference	300	700	300	83.02	21.11	363.00	389.00	√		√	
Reference	300	700	600	92.12	21.95	363.00	389.00	√		√	

Table 3.3b) Various silatrane coating compositions using 0.05 g of silatrane and 4%tot.vol.3-APS

Coating Composition			% Transmittance (λ, nm)			UV Cutoff	Appearance of Surface After Coated			
Acid Catalyst HCl (μL)	Solvent IPA(μL)	Curing Agent GPTS (μL)	780	400	0	@%T=0	Smoothness	Roughness	Transparency	Murky
-*	-*	-*	90.30*	20.50*	361.00*	389.00*	√*		√*	
700	700	300	80.94	20.68	363.00	389.00		√	√	
700	700	600	64.41	16.00	363.00	390.00	√			√
700	1000	300	74.95	18.38	363.00	390.00		√		√
700	1000	600	90.88	23.38	363.00	389.00	√		√	
300	700	300	91.92	22.71	363.00	389.00	√		√	
300	700	600	91.30	22.73	363.00	389.00	√		√	
300	1000	300	90.45	25.50	363.00	389.00	√		√	
300	1000	600	91.89	24.41	363.00	389.00	√		√	

Table 3.3c) Various titanium glycolate coating compositions using 0.05 g of titanium glycolate and 4%tot.vol.3-APS

Coating Composition			% Transmittance (λ, nm)			UV Cutoff	Appearance of Surface After Coated			
Acid Catalyst HCl (μL)	Solvent IPA(μL)	Curing Agent GPTS (μL)	780	400	0	@%T=0	Smoothness	Roughness	Transparency	Murky
700	700	300	77.97	19.99	363.00	389.00		√		√
700	700	600	76.78	17.99	363.00	390.00	√			√
700	1000	300	63.67	17.90	363.00	389.00		√		√
700	1000	600	74.75	18.39	363.00	389.00		√		√
700	1000	1000	91.27	21.87	363.00	389.00	√		√	
300	700	300	77.92	19.93	363.00	389.00		√	√	
300	700	600	89.73	22.78	363.00	389.00	√		√	
300	1000	300	87.82	20.63	363.00	389.00		√	√	
300	1000	600	74.57	18.39	363.00	389.00	√		√	
300	1000	1000	91.42	22.29	363.00	389.00	√		√	

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Table 3.3d) Various zirconium glycolate coating compositions using 0.05 g of zirconium glycolate and 4%tot.vol.3-APS

Coating Composition			% Transmittance (λ, nm)			UV Cutoff	Appearance of Surface After Coated			
Acid Catalyst HCl (μL)	Solvent IPA(μL)	Curing Agent GPTS (μL)	780	400	0	@%T=0	Smoothness	Roughness	Transparency	Murky
700	700	300	62.53	14.33	364.00	390.00		√		√
700	700	600	75.38	18.12	363.00	389.00	√		√	
700	1000	300	65.46	13.28	364.00	390.00		√		√
700	1000	600	73.06	17.51	363.00	390.00	√			√
700	1000	1000	88.38	21.71	363.00	389.00				
300	700	300	89.14	21.91	363.00	389.00	√		√	
300	700	600	83.09	20.86	363.00	389.00	√		√	
300	1000	300	88.38	21.71	363.00	389.00	√		√	
300*	1000*	600*	-	-	-	-	-	-	-	-
300*	1000*	1000*	-	-	-	-	-	-	-	-

* the obtaining solutions before coating are milky

Table 3.3e) Comparison of 0.05 g of each precursor using 300 μLHCl:700 μL IPA:300 μLGPTS:4%3-APS

Solution	Coating Composition			% Transmittance (λ, nm)			UV Cutoff	Appearance of Surface After Coated			
	Acid Catalyst HCl (μL)	Solvent IPA(μL)	Curing Agent GPTS (μL)	780	400	0	@%T=0	Smoothness	Roughness	Transparency	Murky
	TS56DX	-	-	-	90.30	20.50	361.00	389.00	√		√
Reference	300	700	300	83.02	21.11	363.00	389.00	√		√	
Silatrane	300	700	300	91.92	22.71	363.00	389.00	√		√	
Titanium glycolate	300	700	300	77.92	19.93	363.00	389.00		√	√	
Zirconium glycolate	300	700	300	89.14	21.91	363.00	389.00	√		√	

Table 3.2e) comparing all three precursors using the 300 μ L HCl:700 μ L IPA:300 μ L GPTS:4%APS formula shows the rough defect in the case of titanium glycolate. Denials and Francis explained this phenomenon that the rough surface was depended on the amount of GPTS generating various amount of M-OM (M= Si, Ti, Zr) polymer; during drying process the polymer underwent further condensation to form more cross-linked M-O-M polymer phase, and the porosity decreased as M-OR increased. High amount of GPTS may prevent cracks and roughness by allowing stress relaxation before the coating mixture is solidified. As the coated film was getting dried, unabsorbed GPTS materials may form a viscous fluid matrix filling the space between particles, allowing particles to rearrange before the film was fully dried and became rigid. Thus, too low amount of GPTS provided no particle rearrangement due to the presence of more empty spaces between particles.

Effect of Factors on Gellation Time

Gel time is one of those factors demonstrating the rates of hydrolysis and condensation. The shorter gel time indicates the higher hydrolysis and condensation rates.

Effect of Precursor Quantity on the Gellation Time

From figure 3.8, the gellation time of the reference condition (precursor quantity is zero) was shorter than the one containing 0.05 g. of precursors. However, when using 1000 μ l of GPTS, the gellation time decreased as increasing the amount of silatrane or titanium glycolate. The reason is owing to an increase in both the hydrolysis and condensation rates. When adding more precursors most conditions resulted in shorter gellation time in which can be explained by the ratio of organometallic coating composition [30]. The reaction between the acid and each precursor is different in terms of the hydrolysis and condensation rates. Zirconium glycolate shows longer gellation time as increasing the precursor quantity, indicating the slower hydrolysis and condensation rates due to the basic property of the precursor, as observed by pH measurement (pH 9-10), reducing the acid concentration [31].

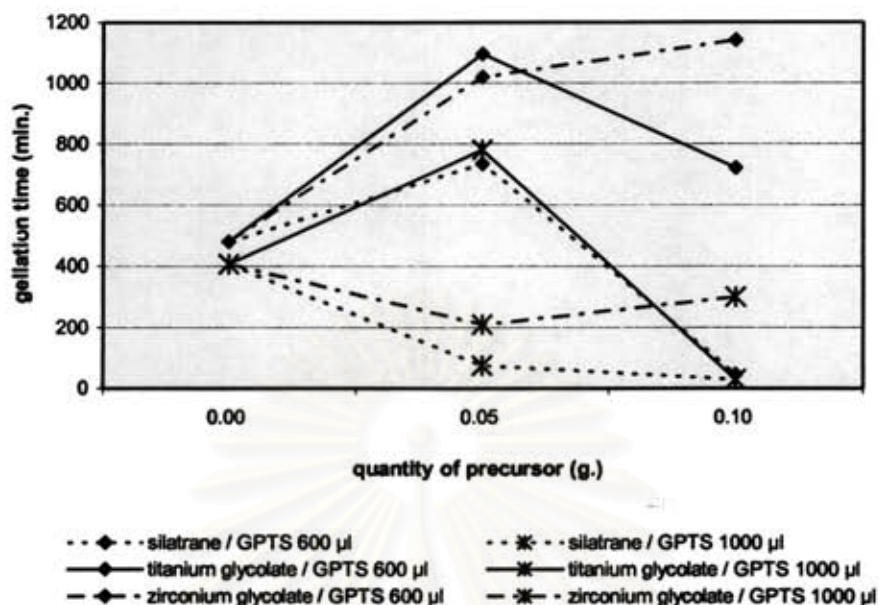


Figure 3.8 Effect of precursor quantity on the gelation time.

Effect of Acid Quantity on the Gelation Time

In the reference case where no acid was added, the gelation time will be longer than 48 h. When increasing the amount of 1M HCl the gelation time decreases, as shown in figure 3.9. The reason is that the acid catalyzes the sol-gel process, causing the decrease in the gelation time.

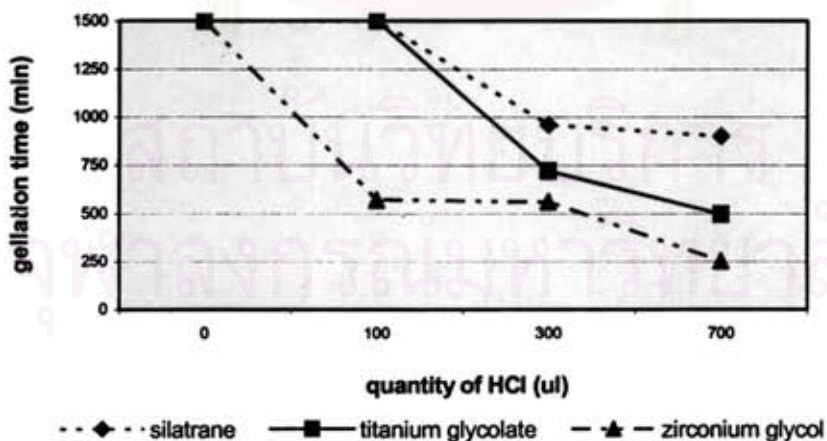


Figure 3.9 Effect of acid quantity on the gelation time.

Effect of Isopropyl Alcohol Quantity on the Gellation Time

From figure 3.10, the higher amount of IPA shows the longer gellation time. It can be described that the higher amount of IPA indirectly reduces the acid strength, the hydrolysis and condensation rates are thus slow.

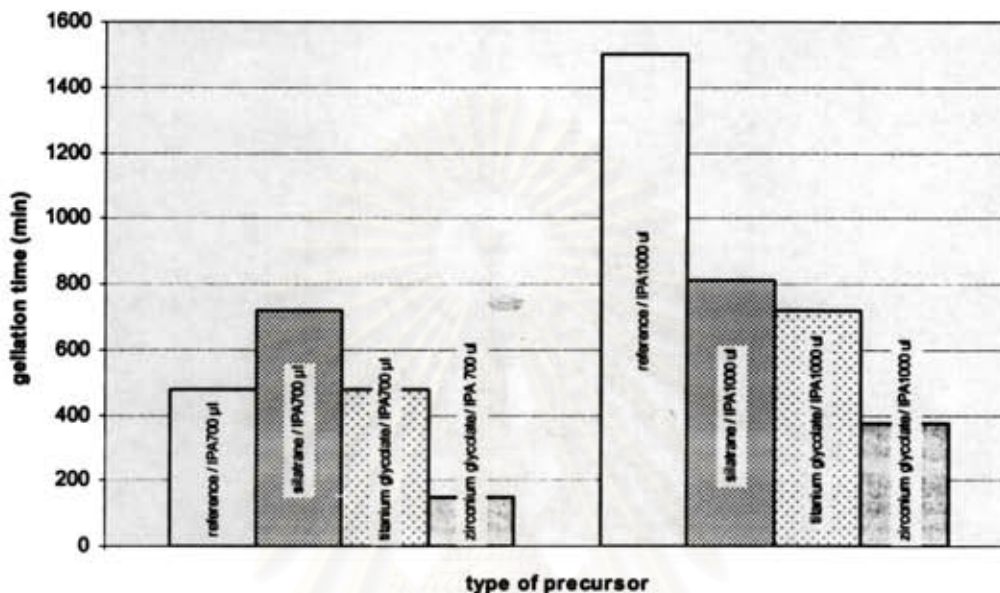


Figure 3.10 Effect of isopropyl alcohol quantity on the gellation time.

Effect of 3-APS Quantity on the Gellation Time

Figure 3.11 shows the results of each precursor when increasing %APS from 3 to 4, 5 and 10%. The precursors in 1000µL of IPA using 3%APS consume a very long time to form gel (more than 48 h). If %APS increases, the gellation time will decrease since APS is acting as the binder to maintain clear sol and also as reactant. When IPA used for surface treatment evaporates rapidly, a portion of 3-APS was partially hydrolyzed and condensed to form a layer on the substrate [12].

Effect of GPTS Quantity on the Gellation Time

As GPTS quantity increased, the methoxy groups (Si-O-CH₃) in GPTS also increased. These groups are rapidly hydrolyzed with acid solution to form silanol group (Si-OH) [22]. The silanol in the hydrolyzed GPTS monomer condensed with each other to produce dimer and larger oligomers containing Si-O-Si bonds. Therefore, higher rates of hydrolysis and condensation occur after adding higher

amount of GPTS, resulting in a decrease in the gellation time, as can be seen in figure 3.12.

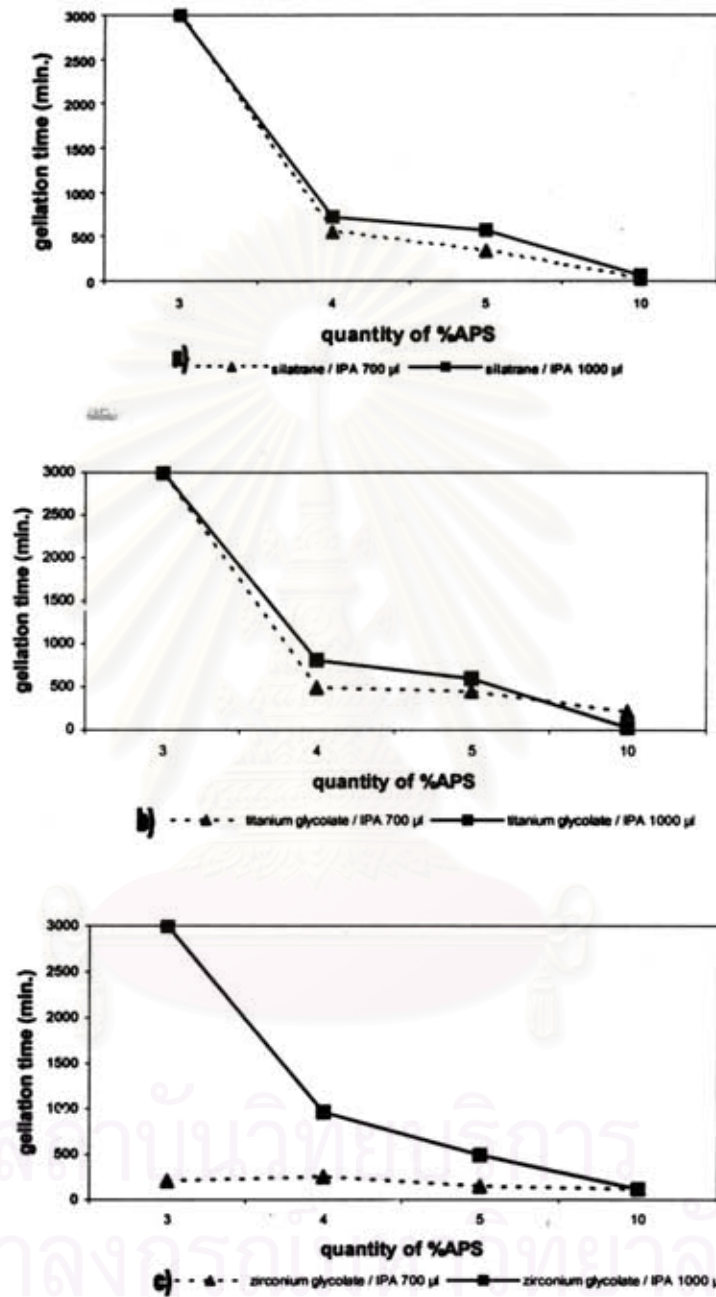


Figure 3.11 Effect of 3-APS on the gellation time of a) silatrane, b) titanium glycolate and c) zirconium glycolate.

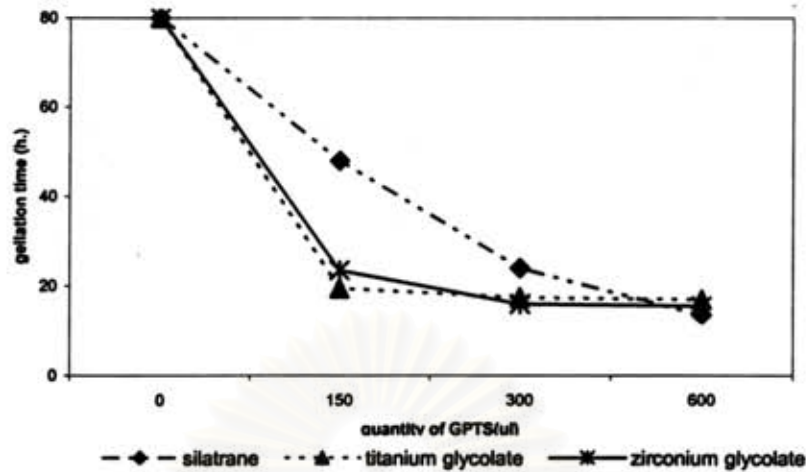


Figure 3.12 Effect of GPTS quantity on the gellation time.

Effect of Type of Precursor on the Gellation Time

In the acid condition, zirconium glycolate coating composition has the shortest gellation time when compared with the other precursors. Different structure of precursor showed different polarity in the solution. Zirconium glycolate contained the highest polarity, thus resulting in the fastest hydrolysis and condensation rates, as shown in figure 3.10.

Effect of Factors on Yellow Index

The reproducibility of the spectral characteristics (reflectal transmission) differs from the precision optical application, which in general needs to adhere to certain tolerance limits with color of the reflection. In ophthalmic lenses, the color is a primary importance. Lens coated onto products must match in color from day to day. The visual perception of the color can be quantified with the L.a.b. color space using the CIE 1931 standard observer where L = luminescence, a = change in color from red to green, b = change in color from yellow to blue. With this reference, lens can be compared to determine how closely the batches are matching each other in perceived residual reflection. [SPIE Vol.1529 Ophthalmic Lens Design and Fabrication (1991/119).

Effect of Acid Quantity on the Yellow Index

The quantity of HCl used in the study results in slight increase in the yellow index. However, in the zirconium glycolate case, as the acid increases beyond 300 μL , the yellow index decreases due to the basic property of zirconium glycolate itself, neutralizing more acid quantity. Figure 3.13 shows the spectrophotometry testing and the calculated yellow index of each precursor in various quantities of HCl, giving different trend. Titanium glycolate mixture was an exceptional case where less than 300 μL of 1M HCl was used. The gel formation did not occur, as discussed in the effect of acid quantity on the gellation time.

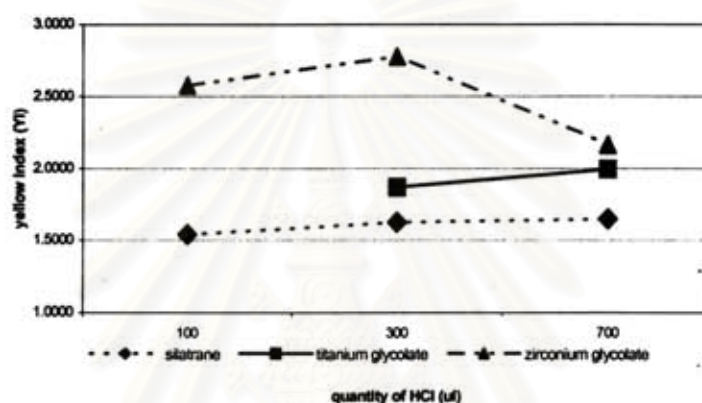


Figure 3.13 Effect of acid quantity on the yellow index.

Effect of IPA Quantity on the Yellow Index

The result shows the yellow index increases as increasing the IPA quantity (figure 3.14). The IPA used as a solvent in the coating material affects to the yellow index, depending on the type of the coating material. 3-APS tended to be oxidized by the air easier when it was dissolved in IPA. Hence, it can be implied that the higher amount of IPA gave the more chance for 3-APS to be oxidized.

Effect of 3-APS Quantity on the Yellow Index

3 APS quantity affected differently to the yellow index results of each precursor, as can be seen in figure 3.15. This might be due to their structural property, resulting in different reactivity toward 3-APS. Silatrane containing amino group is easier to mix with 3-APS while the others are rather difficult, giving more chance for unreacted 3-APS to be decomposed.

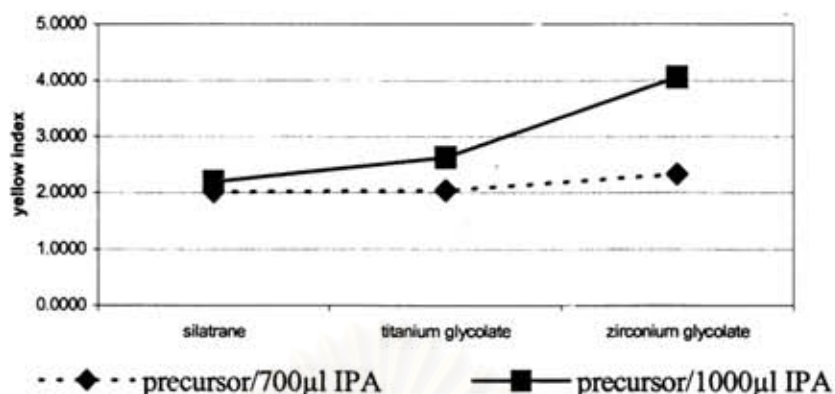


Figure 3.14 Effect of IPA quantity on the yellow index.

Effect of GPTS Quantity on the Yellow Index

All precursors show the same trend of decreasing in the yellow index as increasing the GPTS quantity. For small amount of GPTS, the grafting reaction slightly occurred while the same amount of heat from the oven was applied to the sample. Thus, the heat was too high and caused some decomposition of un-grafted materials, making higher yellow index, see figure 3.16.

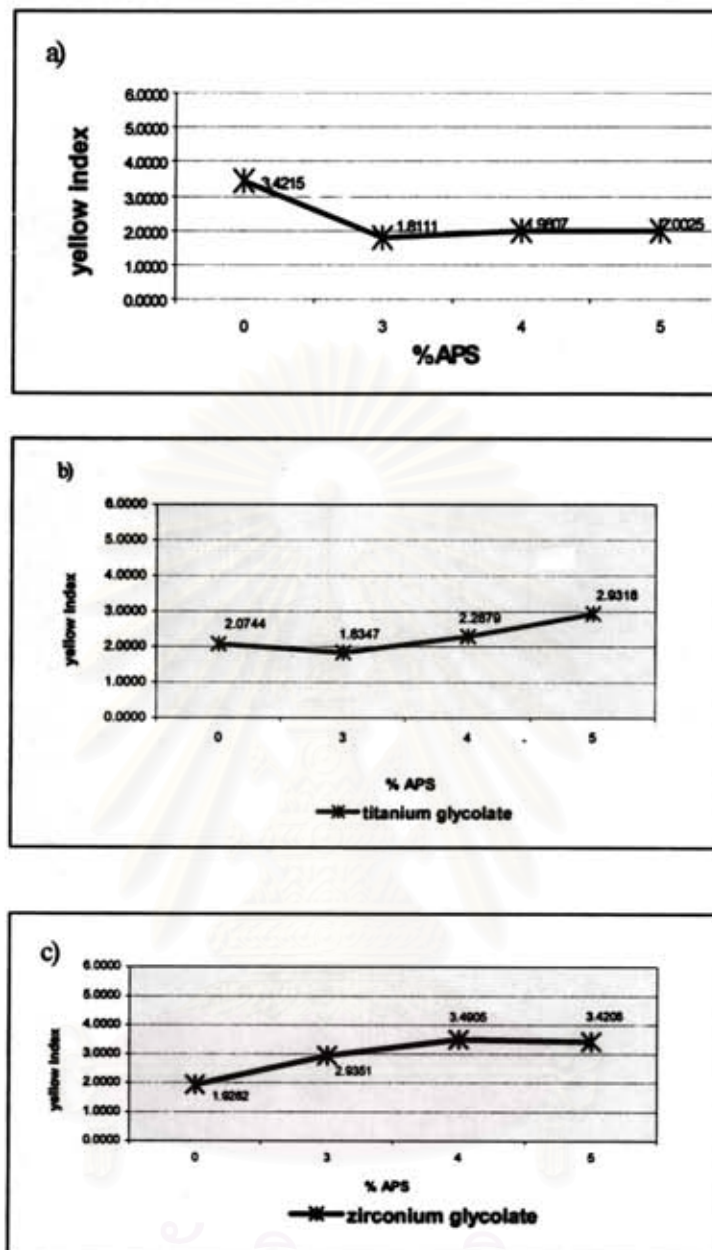


Figure 3.15 Effect of 3-APS quantity on the yellow index.

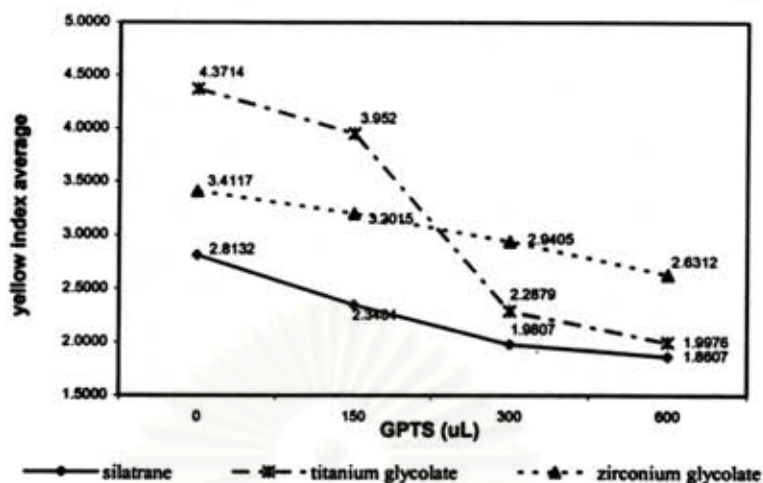


Figure 3.16 The effect of GPTS quantity on the yellow index of silatrane, titanium glycolate and zirconium glycolate.

Effect of Precursor Quantity on the Yellow Index

The quantity of precursor has direct effect on the increasing yellow index, as observed in figure 3.17. However, in the silatrane case, the quantity gave no effect due to the miscibility of silatrane in the coating solution, as discussed previously.

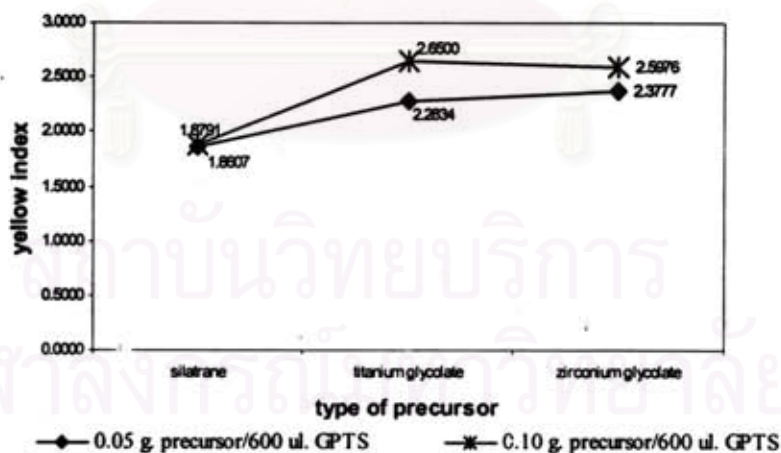


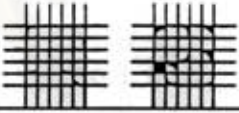
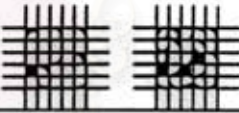
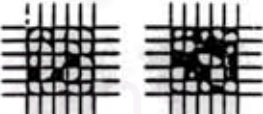
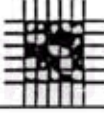


Figure 3.17 The effect of precursor quantity on the yellow index

Effect of Factors on Adhesion Test

The adhesion test is generally needed for determining the efficiency of the film coated onto the substrate by starting with the tape test. The cross-cut tape test evaluates the percent area removed after pulling the tape off. The test results are according to ASTM: D3359-02, and shown in table 3.3.

Table 3.3 Classification of adhesion test

Classification of Adhesion Test Results		
Classification	Percent Area Removed	Surface occurrence of crosscut area for six parallel cuts and adhesion range by percent
5B	0% None	
4B	Less than 5%	
3B	5-15%	
2B	15-35%	
1B	35-65%	
0B	Greater than 65%	

The other method is the boiling water adhesion. This test determines the lens ability to resist moist heat. The test result is observed from any defect, such as,

cracking, crazing, separation, etc., that might occur after boiling for one 15 min/ cycle, (L-12-12-01 boiling Water Adhesion, [32]).

Effect of Acid Quantity on the Adhesion Test

The tape test (table 3.4) shows the corresponding percent area removed as increasing the amount of HCl. When the area was 0% removed, it is categorized in the 5B level. The test results of boiling water adhesion are not as good and not depended on the HCl quantity. The reason is that, in general, the thickness obtained from commercial coatings is about 2 μm , however, in our case, due to the dipping process that was unable to control the thickness, the obtained coating film was more than 5 μm . Each cycle of 15 min boiling thus showed some defect.

Table 3.4 The results of acid quantity on the adhesion test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Adhesion test	
Quantity (g.)	Types	HCl (μL)	IPA (μL)	GPTS (μL)	APS(%/tot vol.)	tape test	boiling water
0.05	silatrane	100	700	300	4	5B	cycle3
0.05	silatrane	300	700	300	4	5B	cycle2
0.05	silatrane	700	700	300	4	5B	cycle3
0.05	Titanium glycolate*	100	700	300	4	-	-
0.05	titanium glycolate	300	700	300	4	5B	cycle1
0.05	titanium glycolate	700	700	300	4	5B	cycle1
0.05	zirconium glycolate	100	700	300	4	5B	cycle3
0.05	zirconium glycolate	300	700	300	4	5B	cycle3
0.05	zirconium glycolate	700	700	300	4	5B	cycle3

* This condition gave milky sol.

Effect of IPA Quantity on the Adhesion Test

Table 3.5 summarizes the capability of hard coating materials. As the IPA quantity increases, the adhesion tape test is better in all of ratios, but the boiling water test shows different cycle of 15 min boiling that resulted in some defect. That means, the boiling water test is independent on the IPA quantity.

Table 3.5 The results of IPA quantity on the adhesion test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Adhesion test	
Quantity (g.)	Types	HCl (μ L)	IPA (μ L)	GPTS (μ L)	APS(%/tot vol.)	tape test	boiling water
0.05	silatrane	300	700	300	4	5B	cycle2
0.05	silatrane	300	1000	300	4	5B	cycle3
0.05	silatrane	700	700	1000	4	5B	cycle1
0.05	silatrane	700	1000	1000	4	5B	cycle1
0.05	titanium glycolate	300	700	300	4	5B	cycle1
0.05	titanium glycolate	300	1000	300	4	5B	cycle1
0.05	titanium glycolate	700	700	1000	4	5B	cycle1
0.05	titanium glycolate	700	1000	1000	4	5B	cycle1
0.05	zirconium glycolate	300	700	300	4	5B	cycle5
0.05	zirconium glycolate	300	1000	300	4	5B	cycle3
0.05	zirconium glycolate	700	700	1000	4	5B	cycle2
0.05	zirconium glycolate	700	1000	1000	4	5B	cycle3

Effect of GPTS Quantity on the Adhesion Test

The results of adhesion test in table 3.6 indicate GPTS independence. However, in the zirconium glycolate case, the higher GPTS amount seemed to affect to the boiling water test. As discussed previously, zirconium glycolate coating solution is in the 8-9 pH range. As described by Song et al, in the basic solution, rapid condensation of hydrolyzed GPTS species was favored to form larger oligomer with

2, 3 siloxane bond. Moreover, they were not absorbed on the substrate, making the condition adhere poorly. Therefore, in our case of zirconium glycolate, when the GPTS amount was increased, coating efficiency was decreased, easily resulting in defect.

Table 3.6 The result of GPTS quantity on the adhesion test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Adhesion test	
Quantity (g.)	Types	HCl (μ L)	IPA (μ L)	GPTS (μ L)	APS(%/tot vol.)	tape test	boiling water
0.05	silatrane	300	700	300	4	5B	cycle2
0.05	silatrane	300	700	600	4	5B	cycle2
0.05	silatrane	700	700	300	4	5B	-
0.05	silatrane	700	700	600	4	5B	cycle1
0.05	titanium glycolate	300	700	300	4	5B	-
0.05	titanium glycolate	300	700	600	4	5B	cycle1
0.05	titanium glycolate	700	700	300	4	5B	cycle1
0.05	titanium glycolate	700	700	600	4	5B	cycle1
0.05	zirconium glycolate	300	700	300	4	5B	cycle4
0.05	zirconium glycolate	300	700	600	4	5B	cycle1
0.05	zirconium glycolate	700	700	300	4	5B	cycle3
0.05	zirconium glycolate	700	700	600	4	5B	cycle4

Effect of 3-APS Quantity on the Adhesion Test

Various quantities of 3-APS do not seem to have any effect on the tape test (table 3.7). All samples showed the tape test in the 5B level. However, as compared with commercial coating solution, the boiling water test results were not as good owing to again the thicker film obtained in this research work. It is worth noting that when the 3-APS was 0%, the coating did not form film, instead it formed small

droplet on the surface, so the test result was not observed its cracking. Addition of 3-APS from 4 to 5 % by total volume can further enhance durability in boiling water, based on the total organic-inorganic network of the solution.

Table 3.7 The result of 3-APS quantity on the adhesion test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Adhesion test	
Quantity (g.)	Types	HCl (μL)	IPA (μL)	GPTS (μL)	APS(%/tot vol.)	tape test	boiling water
0.05	silatrane	300	700	300	0	5B	-
0.05	silatrane	300	700	300	4	5B	cycle1
0.05	silatrane	300	700	300	5	5B	cycle1
0.05	titanium glycolate	300	700	300	0	5B	-
0.05	titanium glycolate	300	700	300	4	5B	cycle2
0.05	titanium glycolate	300	700	300	5	5B	cycle11
0.05	zirconium glycolate	300	700	300	0	5B	-
0.05	zirconium glycolate	300	700	300	4	5B	cycle6
0.05	zirconium glycolate	300	700	300	5	5B	cycle8

Effect of Precursor Quantity on the Adhesion Test

The results in table 3.8 are similar to previous tables. That is, they showed good results for the tape test, but not for the boiling water test. In the silatrane case, the higher silatrane quantity gave the better result for the boiling water test.

Different precursor, silatrane, titanium glycolate and zirconium glycolate, gave no effect on the adhesion by either the tape test or the test in boiling water. In the case of reference, both the tape and boiling water tests were also graded "pass", but the difference is the refractive index value, as discussed in the latter section.

Table 3.8 The result of precursor quantity on the adhesion test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Adhesion test	
Quantity (g.)	Types	HCl (μ L)	IPA (μ L)	GPTS (μ L)	APS(%/tot vol.)	tape test	boiling water
0.05	silatrane	700	1000	600	4	5B	cycle3
0.1	silatrane	700	1000	600	4	5B	cycle5
0.05	silatrane	700	1000	1000	4	5B	cycle1
0.1	silatrane	700	1000	1000	4	5B	cycle2
0.05	titanium glycolate	700	1000	600	4	5B	cycle3
0.1	titanium glycolate	700	1000	600	4	5B	cycle3
0.05	titanium glycolate*	700	1000	1000	4	-	-
0.1	titanium glycolate	700	1000	1000	4	5B	cycle1
0.05	zirconium glycolate	700	1000	600	4	5B	cycle5
0.1	zirconium glycolate*	700	1000	600	4	-	-
0.05	zirconium glycolate	700	1000	1000	4	5B	cycle2
0.1	zirconium glycolate	700	1000	1000	4	5B	cycle4

* The obtained surface was too rough to measure the test.

Effect of Factors on Scratch Test

The scratch test is an important test that needs to be satisfied. In order to compare the abrasion resistance between different coating systems without considering the effect of coating thickness, all damages caused by the steel wool abrasion test must be confined with the coating layer until the end of test, meaning that the coating layer has to be thick enough and the adhesion between coating layer and substrate should be sufficient.

In the previous work [5] the study was used a heavier loading on each abrader wheel (500 g), the scratch test results thus showed no difference. The result showed the coating thickness has little or no influence on abrasion resistance up to at

least 500 cycles. This demonstrates that under the test conditions, the coating thickness range would not be affected.

In this research work, #000 or #0000 grade steel wool was used, and the steel wool is rubbed across the lens surface using a 1.0 kg. (2.2 lbs) force continuously applied for 75 cycles. This rubbing can be done with an oscillating machine, such as, the Sutherland Abrasion tester or by hand. The result is compared with commercial hard coat solution. The standard results are shown in table 3.9.

Table 3.9 The standard test of using steel wool and 500 g force

Level of hardness	Number of scratching line
A	0
B	1-3
C	4-20
D	21-40
E	41-100
F	More than 100

Effect of Acid Quantity on the Scratch Test

Amount of acid does not affect to the scratch test. Each precursor shows different result for different condition, as shown in table 3.10.

Effect of IPA Quantity on the Scratch Test

Table 3.11 shows the scratch test results ranging from grade C to grade E. The data indicate no IPA independence as the conditions were varied.

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Table 3.10 The effect of acid quantity on the scratch test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Coupling agent	Curing agent	Steel wool test	
Quantity (g.)	Types	HCl (μL)	IPA (μL)	GPTS (μL)	APS(%/tot vol.)	Level	No. of scratch line
0.05	silatrane	100	700	300	4	C	10
0.05	silatrane	300	700	300	4	C	5
0.05	silatrane	700	700	300	4	D	21-40
0.05	titanium glycolate	100	700	300	4	milky sol	milky sol
0.05	titanium glycolate	300	700	300	4	C	10
0.05	titanium glycolate	700	700	300	4	C	15
0.05	zirconium glycolate	100	700	300	4	E	41-100
0.05	zirconium glycolate	300	700	300	4	C	10
0.05	zirconium glycolate	700	700	300	4	C	15

Effect of GPTS Quantity on the Scratch Test

As described by Kim et al, the ratio of GPTS molecules to 3-APS was lower, the Raman peak intensity at 1256 cm^{-1} of epoxy bond decreased. The epoxy ring opening of GPTS by 3-APS was easier to attack and polymerization was faster. In this study, the results were in agreement with Kim et al's work. That is, the results were increased as the GPTS:3-APS ratio increased. Table 3.12 shows the effect of GPTS quantity on the scratch resistance. When the ratio of GPTS:3-APS was increased to a high level, the scratch line was thus easily increased. That means, the scratch resistance decreases when the ratio of GPTS:3-APS increases.

Table 3.11 The effect of IPA quantity on the scratch test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Steel wool test	
Quantity (g.)	Types	HCl (μ L)	IPA (μ L)	GPTS (μ L)	APS(%/tot vol.)	Level	No. of scratch line
0.05	silatrane	300	700	300	4	C	5
0.05	silatrane	300	1000	300	4	C	10
0.05	silatrane	700	700	1000	4	E	41-100
0.05	silatrane	700	1000	1000	4	D	21-40
0.05	titanium glycolate	300	700	300	4	C	10
0.05	titanium glycolate	300	1000	300	4	C	8
0.05	titanium glycolate	700	700	1000	4	E	41-100
0.05	titanium glycolate	700	1000	1000	4	C	9
0.05	zirconium glycolate	300	700	300	4	C	5
0.05	zirconium glycolate	300	1000	300	4	C	10
0.05	zirconium glycolate	700	700	1000	4	E	41-100
0.05	zirconium glycolate	700	1000	1000	4	D	21-40

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Table 3.12 The effect of GPTS quantity on the scratch test

Precursors		Organometallic coating composition				Result	
		Acid catalyst	Solvent	Coupling, curing agent	GPTS (μL): % 3-APS	Steel wool test	
Quantity (g.)	Types	HCl (μL)	IPA (μL)	GPTS (μL), % 3-APS	Ratio	Level	No. of scratch line
0.05	silatrane	300	700	300, 4	5.8 : 1	C	5
0.05	silatrane	300	700	600, 4	4.7 : 1	D	21
0.05	silatrane	700	700	300, 4	10.4 : 1	D	21-40
0.05	silatrane	700	700	600, 4	9.3 : 1	E	41-100
0.05	titanium glycolate	300	700	300, 4	5.8 : 1	C	10
0.05	titanium glycolate	300	700	600, 4	4.7 : 1	C	20
0.05	titanium glycolate	700	700	300, 4	10.4 : 1	C	10
0.05	titanium glycolate	700	700	600, 4	9.3 : 1	C	13
0.05	zirconium glycolate	300	700	300, 4	5.8 : 1	C	14
0.05	zirconium glycolate	300	700	600, 4	4.7 : 1	E	41-100
0.05	zirconium glycolate	700	700	300, 4	10.4 : 1	C	15
0.05	zirconium glycolate	700	700	600, 4	9.3 : 1	D	21

Effect of 3-APS Quantity on the Scratch Test

As described previously, 3-APS is used to promote sufficient adhesion between coating film and substrate [5]. According to Kim et al's work, an increase in GPTS concentration under basic conditions would produce more nucleophilic hydroxyl anions which attack the alkoxy silane, thus in this work, only the zirconium glycolate coating solution being basic condition was studied to determine whether increasing GPTS would affect the scratch test. Table 3.13 shows that as the quantity of 3-APS increases, the number of scratch line decreases. The reason is explained that 3-APS is a linker of materials in the system, the higher the 3-APS used, the better the

adhesive film obtained. Meanwhile, after the epoxy rings are opened, the formation of organic/inorganic network is increased, increasing the hardness property on the coated surface.

Table 3.13 Effect of 3-APS quantity on the scratch test

Precursors		Organometallic coating composition				Result	
		Acid catalysts	Solvent	Cupling agent	Curing agent	Steel wool test	
Quantity (g.)	Types	HCl (μ L)	IPA(μ L)	GPTS(μ L)	APS(%/tot vol.)	Level	No. of scratch line
0.05	silatrane	300	700	300	0	F	>100
0.05	silatrane	300	700	300	4	C	10
0.05	silatrane	300	700	300	5	B	3
0.05	Titanium glycolate	300	700	300	0	F	>100
0.05	Titanium glycolate	300	700	300	4	C	18
0.05	Titanium glycolate	300	700	300	5	C	7
0.05	Zirconium glycolate	300	700	300	0	F	>100
0.05	Zirconium glycolate	300	700	300	4	F	>100
0.05	Zirconium glycolate	300	700	300	5	F	>100
0.05	Zirconium glycolate	600	1000	600	4	C	10
0.05	Zirconium glycolate	600	1000	600	5	B	1
0.05	Zirconium glycolate	600	1000	1000	4	D	25
0.05	Zirconium glycolate	600	1000	1000	5	C	15

Effect of Precursor Quantity on the Scratch Test

Table 3.14 shows the results of the scratch test. If the system increased the quantity of precursor, the scratch resistance would increase, because the organic/inorganic network increases, also resulting in an increase in the hardness of the surface.

For the precursor type, the results by the steel wool test show the level B in silatrane and zirconium glycolate coating composition at the condition of 0.05 g precursor:600 μ L HCl:1000 μ L IPA:600 μ L GPTS:5%APS. This is different from titanium glycolate coating composition showing a good result in the level B at the ratio of 0.05 g precursor:600 μ L HCl:1000 μ L IPA:600 μ L GPTS:4%APS.

Table 3.14 Effect of precursor quantity on the scratch test

Precursors		Coating composition				Result	
		Acid catalyst	Solvent	Cupling agent	Curing agent	Steel wool test	
Quantity (g.)	Types	HCl (μ L)	IPA(μ L)	GPTS (μ L)	APS(%/tot vol.)	level	No. of scratch line
0.05	silatrane	300	700	300	4	C	10
0.1	silatrane	300	700	300	4	C	8
0.05	silatrane	700	1000	600	4	D	21-40
0.1	silatrane	700	1000	600	4	C	7
0.05	titanium glycolate	300	700	300	4	C	18
0.1	titanium glycolate	300	700	300	4	milky sol	milky sol
0.05	titanium glycolate	700	1000	600	4	C	17
0.1	titanium glycolate*	700	1000	600	4	-	-
0.05	Zirconium glycolate	300	700	300	4	C	15
0.1	Zirconium glycolate	300	700	300	4	milky sol	milky sol
0.05	Zirconium glycolate	700	1000	600	4	C	12
0.1	Zirconium glycolate*	700	1000	600	4	-	-

*meaning rough surface which can not be checked the properly

Effect of Factors on Refractive Index

Table 3.15 shows the effect of precursor type on the refractive index. Silatrane coating composition gives the lowest refractive index while titanium glycolate coating shows the highest refractive index. Zirconium glycolate shows the



refractive index in the range of 1.6020-1.6057. Different coating composition shows different refractive index and has achieved good refractivity depending on the metal oxide association choice [33].

Table 3.15 Effect of precursor types on the refractive index

Precursor	Organometallic coating composition				Refractive index		
	Acid catalyst	Solvent	Cupling agent	Curing agent	Type of precursor		
Quantity (g)	HCl (μ L)	IPA (μ L)	GPTS (μ L)	APS(%/tot vol.)	Silatrane	Titanium glycolate	zirconium glycolate
0.05	300	700	300	4	1.5798	1.6132	1.6025
0.05	300	1000	600	4	1.5760	1.6050	1.6050
0.05	300	700	1500	4	1.5710	1.6040	1.6020
0.05	300	1000	600	4	1.5920	1.6065	1.6052
0.05	300	1000	600	5	1.5940	1.6043	1.6025
0.05	700	1000	1000	4	1.5800	1.6355	1.6050

As a whole, to explain the above results, these three precursors could be improved to enhance adhesion between the interface of polyurethane substrate and hard coating material. The attack of an amino group from 3-APS molecule to a polyurethane chain causes the chain cleavage into two chains; one chain terminated with a phenol group and the other with a urethane group [19]. The 3-APS forming the amide bond with one of polyurethane became as substrate while GPTS coupling agent was able to form strong bond with both the inorganic precursors and polymer substrates, linking different materials together [12]. Figure 3.18 shows GPTS forming strong bond with inorganic precursor.



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After dipping process, the coating film was pre-cured and post-cured at 60°C and 110°-115°C, respectively, to remove solvent, volatile contents, and to form polymer network. Different concentration caused different coated surface. Some examples using silatrane precursor are shown in figure 3.19. It was found that when less than 600µL of GPTS was used, the obtained surface was not smooth. It is possibly due to the fact that less GPTS amount gave less crosslinked film or thinner film. When applying the same amount of heat, solvent and volatile contents were easier and faster removed, resulting in rougher surface.



Figure 3.19 Polyurethane surface using silatrane precursor coating at a) the concentrations providing smooth surface, and b) the concentration giving rough surface.

The titanium glycolate case gives similar results to those obtained using silatrane, as shown in figure 3.20.

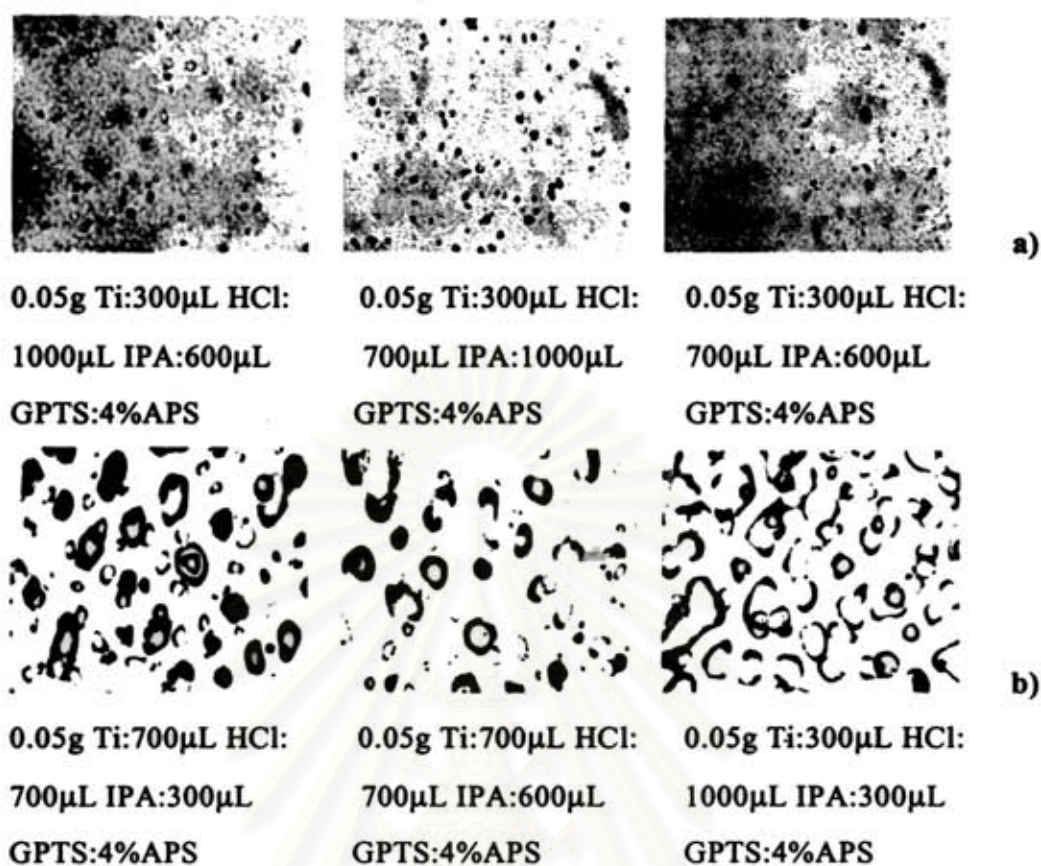


Figure 3.20 Polyurethane surface using titanium glycolate precursor at a) the concentrations giving smooth surfaces, and b) the concentrations giving rough surfaces.

Zirconium glycolate precursor was used in the same manner as a hard coating material. The surface of polyurethane substrate had such a defect in the condition containing higher acid concentration due to the faster hydrolysis and condensation rates causing the faster precipitation of zirconia (figure 3.21).

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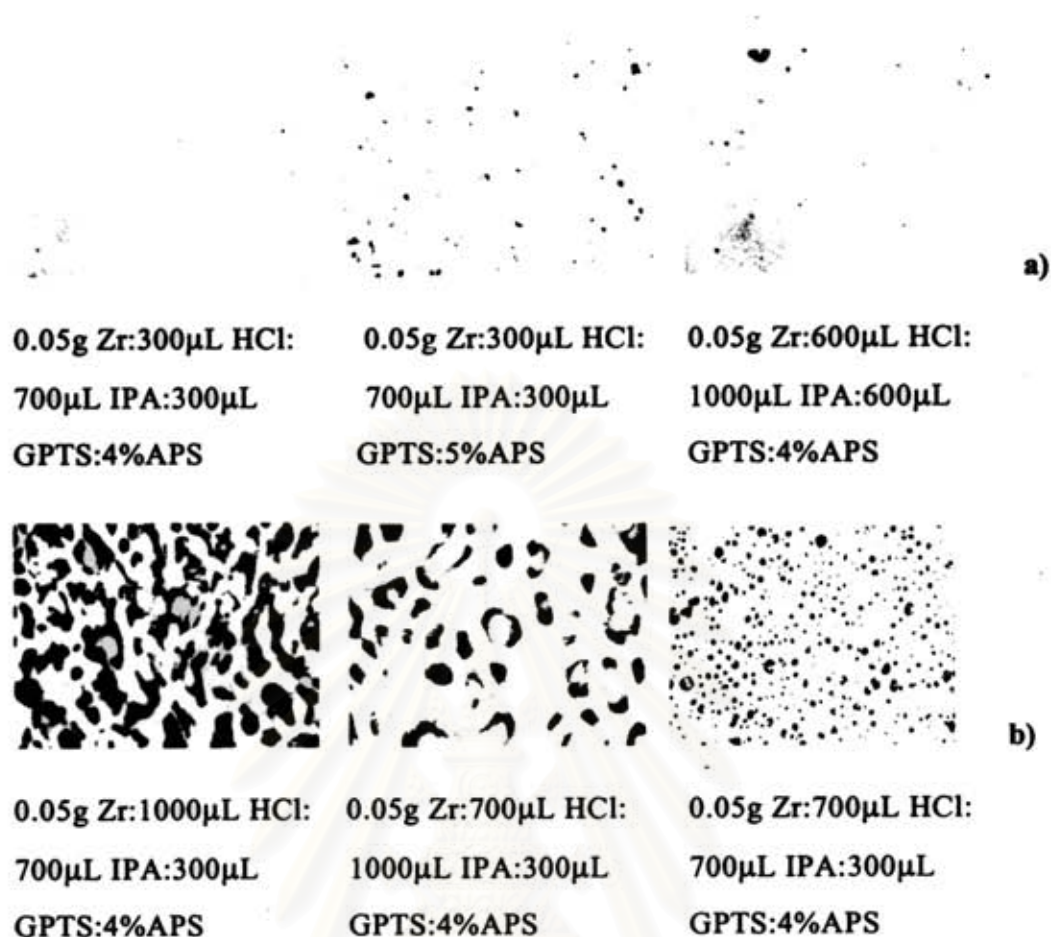


Figure 3.21 Polyurethane surface using zirconium glycolate precursor at a) the concentrations resulting in smooth surfaces, and b) the concentrations giving rough surfaces.

Thickness Measurement Using Scanning Electron Microscope

The scanning electron micrographs were taken to identify the microstructure and the thickness of hard coating films prepared via sol-gel process. Figure 3.22 shows the thickness of silatrane coating film using the 0.05 g silatrane:600 μ L 1M HCl:1000 μ L IPA:600 μ L GPTS:4%3-APS formula. From the SEM results, the thickness of obtained films is in the range of 5.0-8.0 μ m.



Figure 3.22 SEM micrographs of the silatrane coating film thickness.

The thickness of zirconium glycolate coating film was observed using the condition of 0.05g silatrane:600 μ L HCl:1000 μ L IPA:600 μ L GPTS:4%3-APS, as shown in figure 3.23.



Figure 3.23 SEM micrograph of the zirconium glycolate coating film thickness.

The titanium glycolate coating film is as thick as those obtained using silatrane and zirconium glycolate. The thickness was observed from the condition of 0.05 g silatrane:600 μ L HCl:1000 μ L IPA:600 μ L GPTS:5%3-APS, as shown in figure 3.24.



Figure 3.24 SEM micrographs of the titanium glycolate coating film thickness.

The Optimal Condition of Each Precursor

Silatrane, titanium glycolate and zirconium glycolate as the precursors are individually used for coating the ophthalmic lens to compare the coating properties. The optimal condition for silatrane provides the best property while zirconium glycolate precursor shows the highest scratch resistance using the precursor:HCl:IPA:GPTS:%APS ratio of 0.05g:600 μ L:1000 μ L:600 μ L:5%. In case of titanium glycolate precursor, the optimal ratio is 0.05g precursor:600 μ LHCl:1000 μ LIPA:600 μ LGPTS:4%3-APS. All of these results give good and properties, as shown in table 3.16.

Table 3.16 The test results of the optimal condition of each precursor

Precursor	Results						
	Gel time (h)	%T@ $\lambda=780$ nm.	Y.I.	Adhesion test		Abrasion test	R.I.
				Tape test	Boiling water		
silatrane	10	91.45	1.780	5B	3	B=1	1.587
titanium	6	87.59	2.064	5B	5	B=1	1.602
zirconium	14	90.49	1.998	5B	3	B=3	1.605
TS56	-	90.30	2.260	5B	>5	A,B	1.602

CHAPTER IV

Conclusions and Recommendations

The hard coated film on polyurethane substrate can be prepared using a mixture of hydrophilic coating solution containing primer solution of 3-amino propyltriethoxysilane, glycidoxypropyltrimethoxysilane (GPTS) and partially hydrolyzed metal alkoxide precursor via the sol-gel process. Silatrane, titanium glycolate and zirconium glycolate as the precursors are individually used for coating the ophthalmic lens to compare the coating properties. Using the precursor:HCl:IPA: GPTS:%APS ratio of 0.05g: 600 μ L:1000 μ L:600 μ L:5%, silatrane provides the best property while zirconium glycolate precursor shows the highest scratch resistance and is categorized as level B (number of scratch line is equal to 1). Adhesion by tape test of both precursors is graded as level 5B. However, their refractive index values are different, silatrane shows lower value. In the case of titanium glycolate precursor, the optimal ratio is 0.05g:600 μ L:1000 μ L:600 μ L:4%APS. It gives the highest durability in scratch test and adhesion by tape test. The level of hardness after testing was graded as level B (number of scratch line is equal to 3). The tape does not remove the film, thus it is graded as level 5B. All of these results are considered to be good. Uncoated polyurethane shows number of scratch line more than 100, which is categorized as level F. Moreover, when compared with the commercial hard coating solution, our results are nearly the same.

All of conditions studied have both advantages and disadvantages. The solid content in the suitable condition is approximately 28-30%, depending on the solvent quantity. The film appearance is clear and transparent when using low acid and high isopropyl alcohol quantity. The GPTS quantity must also be higher than the acid quantity. The scratch resistant test exhibits a good result when using high concentration of 3-APS. The coating materials prepared using lower GPTS concentration, but higher 3-APS concentration can improve the durability in boiling water and give strong adhesion by tape test. Type of precursor results in different refractive index values. Both zirconium glycolate and titanium glycolate provide higher index lens than silatrane. They improve the indices of lens to high index. Titanium glycolate shows the highest refractive index, 1.6020-1.6355.

From the obtained results it is indicated that these three precursors provide specific properties at different condition. Furthermore, only small quantity of coating solution is successfully prepared, resulting in difficult coating the solution on the substrate during the dipping process. To be applied in industries, pilot scale must be studied.



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REFERENCES

1. Solar International Holdings Ltd. (1996), Surface and Coatings Technology, **81**, 79-86.
2. Chenghong, L., Kurt, J., Garth, L.W. (2000), Abrasion-resistant coatings for plastic and soft metallic substrates by sol-gel reactions of a triethoxysilylated diethylenetriamine and tetramethoxysilane, Wear, **242**, 152-159.
3. Shoichiro, Y., Keisuke, I., Kimio, K. (1998), Physical properties and structure of organic-inorganic hybrid materials produced by sol-gel process, Materials Science and Engineering C, **6**, 75-90.
4. Yang, Y.Y., Ching, Y.C., Wen, C.C. (2003), Synthesis and characterization of organic-inorganic hybrid thin films from poly(acrylic) and monodispersed colloidal silica. Polymer, **44**, 593-601.
5. Wen, J., Vasuddevan, V.J., Wilkes, G.L. (1995), Abrasion resistant inorganic/organic coating materials prepared by sol-gel method, Journal of Sol-Gel Science and Technology, **5**, 115-126.
6. Wenxiu, Q., Sun, Z., Zhou, Y., Lam, Y.L., Cheng, Y.C., Chan, Y.C., Kam, C.H. (2000), Materials Letters, **42**, 326-330.
7. Bohling, D., Coda, M., Blacker, R., Burton, C., Gove, R. (2000), Abrasion resistant and optical thin film coatings for ophthalmic lenses, 43rd Annual Technical Conference Proceeding-Denver, April 15-20, 222-229.
8. Chul, H.K., Je, H.K., In, S. J., Hyunmin, S., Ki, H.Y. (2003), Preparation and characterization of TiO₂-SiO₂ nano-composite thin films, Ceramics International, 1-6.
9. Yang, L., Cheng, J. (1989), Preparation and characterization of zirconium oxide coatings prepared from ZrCl₂(OC₂H₅)₂ by the sol-gel process, Journal of Non-crystalline Solids, **112**, 442-448.
10. Dan, Y., Chen, S.Y., Lian, T.J. (2003), Surface structure and properties of water-based polymer coating materials prepared by the complexation of two polymer lattices with chemically complementary, Journal of Applied Polymer Science, **90**, 1748-1754.

11. Winkler, R.P., Arpac, E., Schirra, H., Sepeur, H., Wegner, I., Schmidt, H. (1999), Aqueous wet coatings for transparent plastic glazing, Thin Solid Films, 209-211.
12. Kim, D.H., Moon, J.H., Lee, D.W., Shul, Y.G. (2003), Investigation of the curing mechanism in the GPTS/APTS binder system, Journal of Sol-Gel Science and Technology, 26, 403-406.
13. Choroenpinijkarn, W., Suwankruhasn, M., Kesapabutr, B., Wongkasemjit, S., Jamieson, A.M. (2001), Sol-gel process of silatrane, European Polymer Journal, 37, 1441-1448.
14. Phonthammachai, N., Chairassameewong, T., Gulari, E., Wongkasemjit, S. (2001), Oxide One Pot Synthesis of a Novel Titanium Glycolate and Its Pyrolysis, J. Met. Mat. Min. 12, 23.
15. Lisa, C.K., Sol-Gel Process, Engineered Materials Handbook, Ceramics and Glasses, ASM International the Materials Information Society, USA, 4, 209-213.
16. Chenghong, L., Garth, L., Wilkes, (1998), The mechanism for 3-amino-propyltriethoxysilane to strengthen interface of polycarbonate substrates with hybrid organic-inorganic sol-gel coatings, Journal of Inorganic and Organometallic Polymer, 8(1), 33-45.
17. Ksapabutr, B., Gulari, E. and Wongkasemjit, S. (2003), "One-Pot Synthesis and Characterization of Novel Sodium Tris(glycozirconate) and Cerium Glycolate Precursors and Their Pyrolysis", Materials Chemistry and Physics, 83/1, 34-42.
18. Man, S.L, Nam, J.J. (2002), Coating of methyltriethoxysilane-modified colloidal silica on polymer substrates for abrasion resistance, Journal of Sol-Gel Science and Technology, 24, 175-180.
19. Li, C., Jordens, K. and Wilkes, G.L. (2000), Abrasion-resistant coatings for plastic and soft metallic substrates by sol-gel reactions of a triethoxysilylated diethylenetriamine and tetramethoxysilane, Wear, 152-159, 242.
20. Urreaga, J.M., Matias, M.C., Lorenzo, V. and Orden, M.U. (2000), Abrasion resistance in the Tumble test of sol-gel hybrid coatings for ophthalmic plastic lenses. Materials Letters, 293-297, 45.

21. Harvey, J.L., et al. (1999), Composition for providing an abrasion resistant coating on a substrate, United States Patent, 19, 6,001,163.
22. Ki, C.S., Jung, K.P., Hyun, U.K., Sung, H.K. (2003), Synthesis of hydrophilic coating solution for substrate using glycidoxypropyltrimethoxysilane, Journal of Sol-Gel Science and Technology, 27, 53-59.
23. Steven, R.D., Adrian, R.B., Alan, A. (2003), Formation of silica/epoxy hybrid network polymers, Journal of Non-Crystalline Solids, 315, 197-205.
24. Yunfa, C., Lianming, J., Yusheng, X. (1998), Sol-gel processing of organic-inorganic nanocomposite protective coatings, Journal of Sol-Gel Science and Technology, 13, 735-738.
25. Daniels, M.W., Francis, L.F. (1998), Silane adsorption behavior, microstructure, and properties of glycidoxypropyltrimethoxysilane-modified colloidal silica coatings, Journal of Colloid and Interface Science, 204, 191-200.
26. Ksapabutr, B., Gulari, E. and Wongkasemjit, S. (2004), "Preparation of Zirconia Powders by Sol-Gel Route of Sodium Glycozirconate Complex", Powder Technology, In press.
27. Phonthammachai, N., Chairassameewong, T., Gulari, E., Jamieson, A.M. and Wongkasemjit, S. (2003), Structural and Rheological Aspect of Mesoporous Nanocrystalline TiO_2 via Sol-Gel Process and Its Rheological Study, Mesoporous and Microporous. Mater., 66/2-3, 261-271.
28. Lin, Y., and Jijian, C. (1989). Preparation and characterization of zirconium oxide coatings prepared from $\text{ZrCl}_2(\text{OC}_2\text{H}_5)_2$ by the sol-gel process. Journal of Non-crystalline Solids, 112, 442-448.
29. Song, K.C., Park, J.K., Kang, H.K., and Kim, S.H. (2003). Synthesis of hydrophilic coating solution for substrate using glycidoxypropyl trimethoxysilane. Journal of Sol-Gel Science and Technology, 27, 53-59.
30. Klein, L.C. Sol-Gel Process. Engineered Materials Handbook, Ceramics and Glasses, ASM International the Materials Information Society, USA . 4, 209-213.

31. Apphakvan, T. (2003), Studies of parameters affecting sol-gel process of sodium tris(glycozirconate) toward the preparation of ZrO_2 . MS Thesis. The Petroleum and Petrochemical College, Chulalongkorn University.
32. Colts-Laboratories. (1997). Boiling water adhesion. Colts standard test, L-12-12-01, 1-5.
33. Floch H.G., Priotton J.J. (1989). Optical coatings prepared from colloid media. Thin Solid Films, 175, 173-178.



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