

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Sol-gel process

A process that has, in the past years, gained much notoriety in the glass and ceramic fields is the sol-gel reaction. This chemistry produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. Although first discovered in the late 1800s and extensively studied since the early 1930s, a renewed interest surfaced in the early 1970s when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process. Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures, as opposed to the much higher melting temperatures required in the production of conventional inorganic glasses. The specific uses of these sol-gel produced glasses and ceramics are derived from the various material shapes generated in the gel state, i.e., monoliths, films, fibers, and monosized powders. Many specific applications include optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers, and catalysts [7-8].

The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process, often mixed with TEOS.

At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. This general reaction scheme can be seen in Figure 2.1.

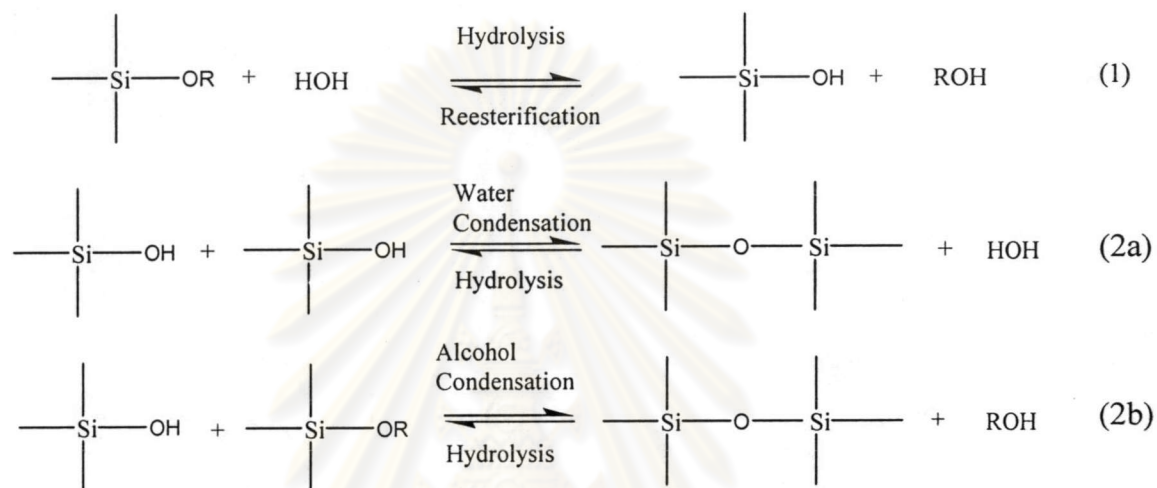


Figure 2.1 The general reaction in sol-gel process [8].

Generally speaking, the hydrolysis reaction (Eq. 2), through the addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions (Eqs. 2a and 2b) involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si) plus the by-products water or alcohol. Under most conditions, condensation commences before hydrolysis is complete. However, conditions such as, pH, H₂O/Si molar ratio and catalyst can force completion of hydrolysis before condensation begins. Additionally, because water and alkoxides are immiscible, a mutual solvent such as an alcohol is utilized. With the presence of this homogenizing agent, alcohol, hydrolysis is facilitated due to the miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate, or inter-knit into a network, a gel is formed. Upon drying, trapped volatiles (water, alcohol, etc.) are driven off and the network shrinks as further

condensation can occur. It should be emphasized, however, that the addition of solvents and certain reaction conditions may promote esterification and depolymerization reactions according to the reverse of Eqs (1), (2a), and (2b) [9].

2.1.1 The advantages of the sol-gel process

- 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 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:-

- 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 occur 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.

2.1.2 Surface improvement using 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 substrates. 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 substrates, 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 used higher temperature, the substrates would crack or striation due to collapse of the gel network.

In general, the coating process in the company most widely uses the dipping method. An overview of the sol-gel process is presented in a simple graphic work below.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

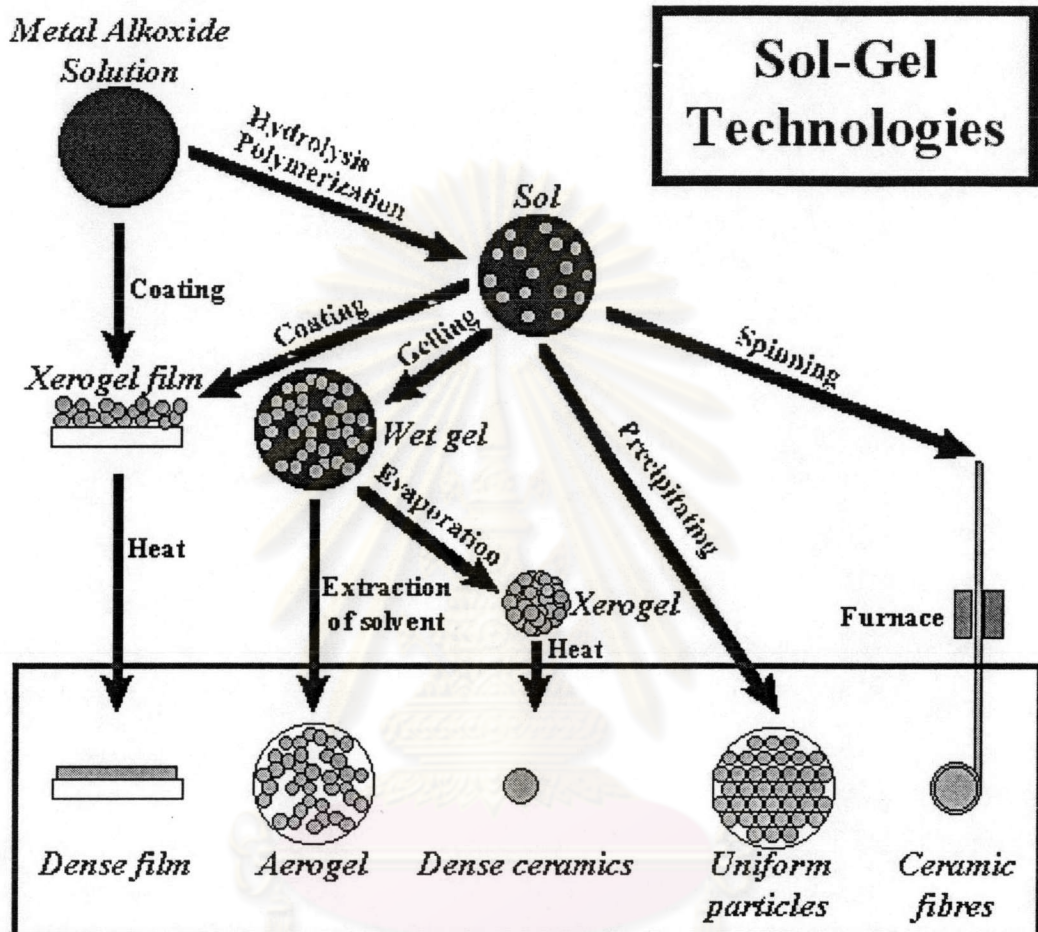


Figure 2.2 An overview of the sol-gel process [8]

2.2 Sol-Gel Coating Method [10]

Several methods can be used to make sol-gel coatings with the sol-gel process. Spin coating and dip-coating are two basic techniques used to deposit sol-gel coatings. Spin coating produces a one-sided coating, while dip coating yields a double-sided coating. Both techniques are used in manufacturing to make different coatings and thin film.

Roll coating is another coating technique and is widely used for industrial coatings, especially for flexible substrates. It can make coatings at a speed of up to 200 ft per minute.

2.2.1 Spin Coating.

Spin Coating is used for many applications where relatively flat substrates or objects are coated with thin layers of material. For example, several cathode ray tube (CRT) manufactures use the spin coating method to make anti-glare or anti-reflection coatings. In spin coating, the material to be made into coating is dissolved or dispersed into a solvent, and this coating solution is then deposited onto the surface and spun off to leave a uniform layer for subsequent processing stages and ultimate use. Figure 2.3 shows a spin coater for general applications.

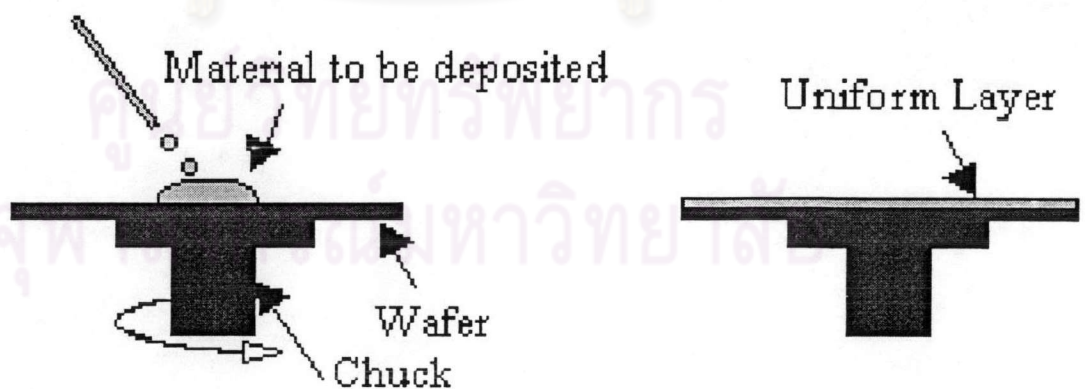


Figure 2.3 Principle of varnishing by spin coating [10]

2.2.2 Dip Coating.

Dip Coating is a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. Vibration-free mountings and very smooth movement of the substrate is essential for dip systems. An accurate and uniform coating thickness depends on precise speed control and minimal vibration of the substrate and fluid surface. The coating thickness is mainly defined by the withdrawn speed, the solid content and the viscosity of the liquid. Figure 2.4 shows a dip coater for general applications.

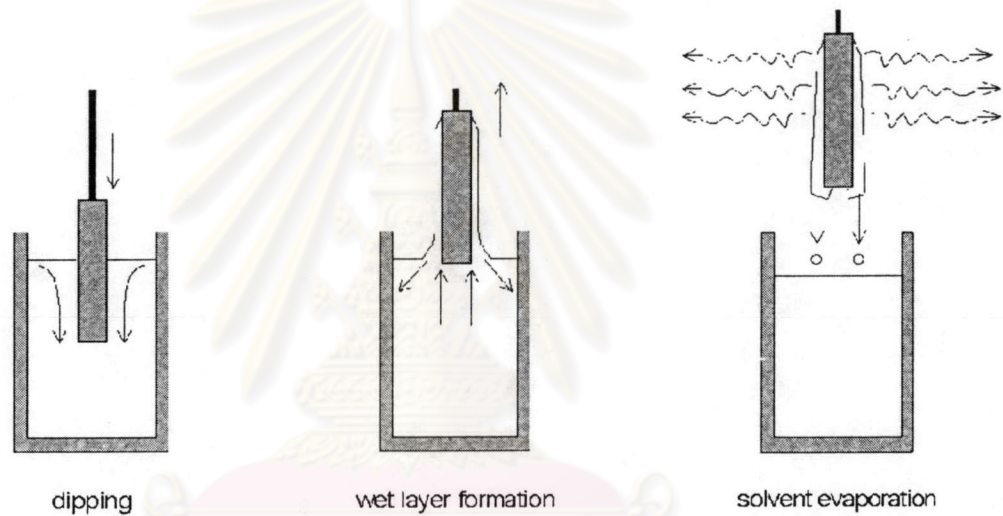


Figure 2.4 Principle of varnishing by dip coating [10]

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

2.3 Literature Review

2.3.1 Metal alkoxide precursor

Charoenpinijkarn *et al.* [11] 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).

2.3.2 Coating materials

Lee M.S. and Jo N.J. [6] 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.* [12] 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 minutes up to 20 hours 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 *et al.* [3] studied the abrasion in the tumble test of PC sheet coated with different acrylic hybrid materials, viz. tetraethoxysilane (TEOS), 3-methacryloxypropyltrimethoxysilane (MPTS) 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 hours. However, the polymerization was almost complete after curing these acrylic coatings for 8 hours. The poor abrasion resistance of samples cured at 120°C for 24 hours, or

at 140°C for 8 hours, 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.

Harreld *et al.* [13] 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 transparency. 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.

Li C. and Wilkes G.L. [14] observed a chemical bonding mechanism based on aminolysis of the carbonate groups by 3-aminopropyltriethoxysilane (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 isopropanol (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.

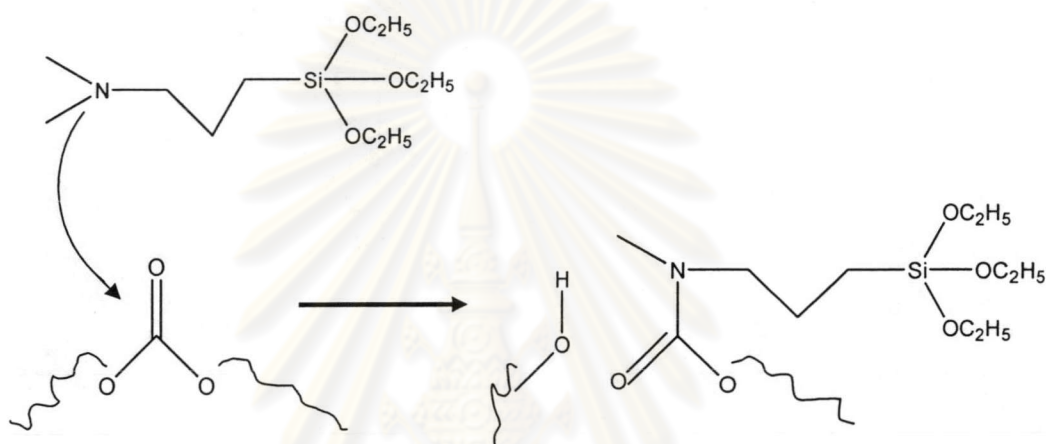


Figure 2.5 The covalent bonding of a layer of alkoxy silane-containing sol-gel coating on the modified polycarbonate substrate [14].

Wen *et al.* [15] 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 isopropanol (IPA) containing 3-aminopropyltriethoxysilane (3-APS). Testing showed strong hydrogen bonding between ester group in polycarbonate substrate and amino group of 3-APS.

2.3.3 Hydrophilic coating solution

Song *et al.* [16] synthesized inorganic-organic hybrid coating solutions with both long-term hydrophilic and crack-free properties by mixing a silane coupling agent, glycidoxypropyltrimethoxysilane (GPTS) 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 GPTS had a profound effect on chemical structure of the coating solutions and hydrophilic property of the coating films. Si-NMR spectroscopic studies showed that the solution prepared under an acid condition (pH 4) consisted of hydrolyzed GPTS monomers without siloxane bond and dimer with one siloxane bond, whereas a basic condition (pH 9.6) was made up larger oligomers with two or three siloxane bonds. In especial, in the case of coating films prepared under highly acidic conditions (pH 1 and 2), the contact angles were less than 5° , which was super-hydrophilic.

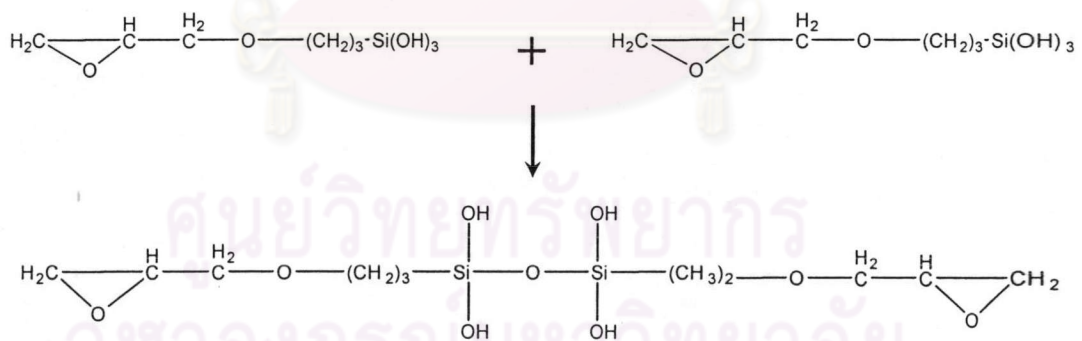


Figure 2.6 Condensation of silanols in hydrolyzed GPTS monomers to produce dimer and larger [16].

Dan *et al* [17] studied water-based polymer coating materials used for the low 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.

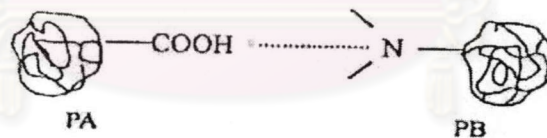


Figure 2.7 Schematic diagram of the interparticle interaction through the hydrogen bonding of the $-\text{COOH}$ group in PA with the $-\text{N}-$ group in PB [17].

Kim *et al.* [18] prepared APTS binder, maintaining clear sol and used as reactant for mixed binder, GPTS/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 APS. On the other hand, for the two-step process, only 8.7% of epoxy ring was opened by amino group of APS. 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 *et al* [19] prepared a number of epoxy-silica hybrid materials by sol-gel/amine curing reaction of GPTS for use in coating on steel. The precursor molecule possessed both epoxy and silicon alkoxide functionality and interlinked inorganic-organic networks was formed. GPTS can undergo a variety of reactions during the preparation of a hybrid by a sol-gel route. Pre-hydrolysis of GPTS 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 T³-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 *et al.* [20] 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 *et al.* [21] 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. [22] investigated the adsorption of GPTS onto silica colloids (20 nm diameter) suspended in an isopropanol/water solution. Coating microstructures consisted of packed colloids with varying amounts of a GPTS siloxane polymer on colloid surface and filling in porosity. When the amount of GPTS added just surpassed that needed to fill the pores (up to $R=0.5$ by weight ratio); 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 GPTS content, but deteriorated when the GPTS content was far in excess of that needed to fill the pores.



คุรุพันธ์วิทยภัทรพยากร
จุฬาลงกรณ์มหาวิทยาลัย