CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

Bis[3-(triethoxysilyl)propyl]tetrasulfide (Si-69) and fumed silica AEROSIL 300; surface area 300 m^2/g, particle size 7 nm, were supplied by JJ. Degussa, Thailand. Hexane, ethanol, benzene (AR grade), and tetrahydrofuran (HPLC grade) were purchased from J.T. Baker Inc.(Phillipsburg, USA.); 1,4-dioxane from CARLO ERBA REAGENTI (Australia); isopropanol from Ajax Chemicals. All chemical reagents were used without purification. Silica is heated at 400^{o}C for 5 h before use.

3.2 Instruments and Equipments

3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained by VECTOR 22 Bruker Spectrometer equipped with deuterated triglycine sulfate (DTGS) detector. A transmission mode was used with 64 scans and 4 cm^{-1} resolution to obtain and analyze quantitatively FTIR spectra of chemisorbed silane onto silica. The treated silica was prepared as a wafer for analysis. Quantitative analysis was operated by OPUS 2.2 program.

3.2.2 Size Exclusion Chromatography (SEC)

SEC chromatograms were performed by Waters GPC 600E attached with RI and UV detectors (Waters 410 and 486, respectively). The separating columns were HR0.5 and HR1 which can separate the molecular weight species from 50-1,000 and 100-5,000, respectively. The absorbance at 254 nm was used for determination of the amount of physisorbed silane by the UV detector.

3.2.3 Ultrasonic Bath

The mixture of silane and silica in each media was reacted in ultrasonic bath, UR1 Retch, for 10 min.

3.2.4 Shaking Water Bath

The suspension mixture was left in shaking water bath, Hetofrig CB60VS, after ultrasonic treatment to undergo the reaction between silane and silica.

3.2.5 High Speed Refrigerated Centrifuge

PM180R High Speed Refrigerated Centrifuge was applied in two steps for separating treated silica from the solution. In the first step, the centrifuge system was used for separating treated silica from unreacted silane. In another step, the centrifuge system was applied to separate physisorbed silane from treated silica with THF solvent.

3.3 Methodology

This study focused on two parameters that influence the amount of deposited silane onto silica: media polarity and silane concentration.

3.3.1 Media Polarity Effect

For the study on media polarity parameter, five media: ethanol, isopropanol, dioxane, benzene, and hexane, are used for investigating the media polarity effect on the chemisorbed and physisorbed silanes. Sample was prepared from a theoretical monolayer of silane to a certain amount of silica, fumed silica 0.15 g, and media 10 mL, by the variation of media types.

3.3.2 Silane Concentration Effect

In order to prepare sample with various amount of silane concentration onto silica, theoretical amount of silane monolayer was calculated. Surface area of silane γ-MPS [CH_2=C(CH_3)COO(CH_2)$_3$Si-(OCH_3)$_3$] was reported to be 60 $\overset{0}{A}^2$. However, the silane Si-69 is nearly twice of the γ-MPS so the silane surface area in this case could be estimated to be 100 $\overset{0}{A}^2$.

Theoretical amount of silane monolayer calculation:

The amount of silane monolayer (g)

$$= \frac{\text{surface area of silica} \times 10^{20} \times \text{molecular weight of silane}}{6.02 \times 10^{23} \times \text{surface area of silane}}$$

$$= \frac{300\ (m^2/g) \times 10^{20} \times 539}{6.02 \times 10^{23} \times 100\left(\overset{0}{A}^2\right)}$$

$$= 0.269 \text{ g of silane / g of silica}$$

For the silane concentration effect, the concentration was varied from less than monolayer to three layers according to the theoretical calculation which can be summarized as shown in Table 3.1.

Table 3.1 Sample formulation for silane treatment as a function of silane concentration

Silane Concentration (Number of Layers)	Silane (g)	Fumed Silica (g)	Media (mL)*
0.005	2.02×10^{-4}	0.15	10.00
0.010	4.04×10^{-4}	0.15	10.00
0.050	2.02×10^{-3}	0.15	10.00
0.100	4.04×10^{-3}	0.15	10.00
0.200	8.07×10^{-3}	0.15	10.00
0.400	1.61×10^{-2}	0.15	10.00
0.800	3.23×10^{-2}	0.15	10.00
1.000	4.04×10^{-2}	0.15	10.00
2.000	8.07×10^{-2}	0.15	10.00
3.000	1.21×10^{-1}	0.15	10.00

* Two types of media, ethanol and hexane, are used.

3.3.3 Procedure

Silane Treatment onto Silica Surface

Sample preparation was done as follows. Silane, media, and fumed silica were added into centrifuge tube and the tube was placed in ultrasonic bath for 10 min to accelerate the silane-silica reaction. Then, the mixture was shaken in water bath at 25°C for 15 min. The obtained suspension was centrifuged at 10,000 rpm for 20 min. Then the supernatant solution was discarded. The precipitate (treated silica) was vacuum dried at room

temperature. After 14 h, the treated silica was heated at 110°C for 15 min to remove the remaining solvent. The reaction of silane onto silica is shown in Figure 3.1.

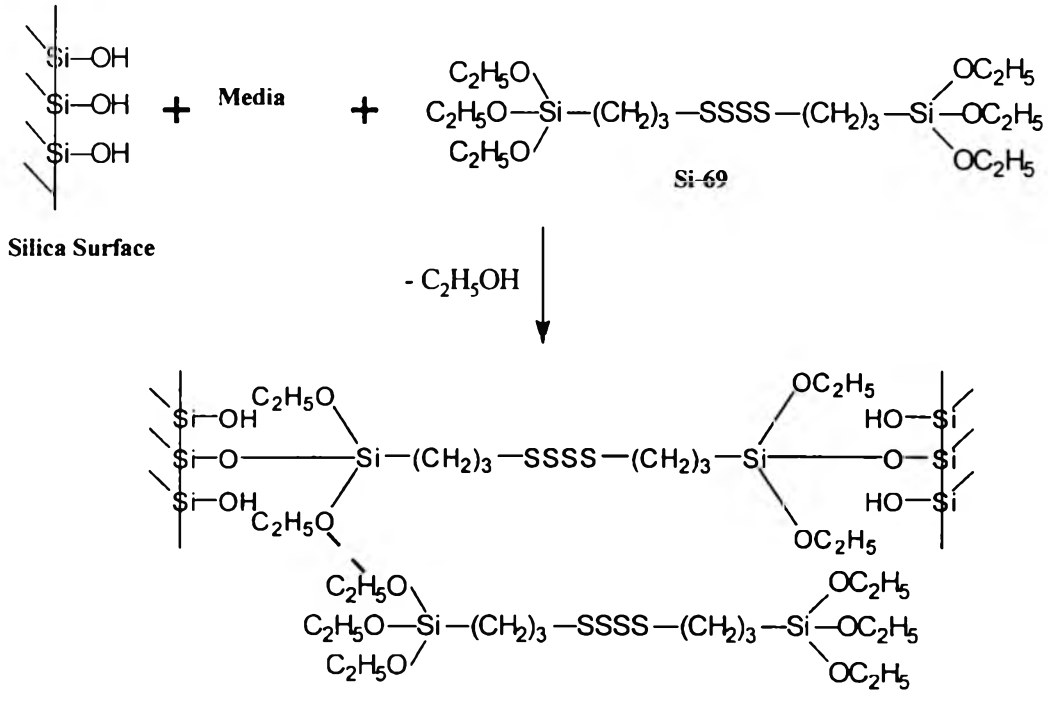

Figure 3.1 Schematical reaction for sample preparation.

3.3.4 Sample Preparation for the Analysis of Chemisorbed and Physisorbed Silanes

After the treated silica was dried thoroughly, the treated silica was stirred in 5 mL tetrahydrofuran (HPLC grade) for 2 h to dissolve the physisorbed silane. After stirring, the suspension was centrifuged at 10,000 rpm for 20 min. The precipitate was repeatedly stirred in 10 mL of THF to completely remove the remained physisorbed silane. The supernatant that contained the physisorbed silane in THF was filtered to remove fine particles of silica, and analyzed by size exclusion chromatography (SEC) technique. The remained silica was dried in vacuum at room temperature for 16 h. Finally, the

silica was ground and vacuum dried at room temperature for 20 h to completely remove the remained solvent. The treated silica was analyzed by quantitative FTIR to observe chemisorbed silane.

3.3.5 Sample Characterization

a) Characterization of the Chemisorbed Silane. Quantitative FTIR was applied to analyze chemisorbed silane. The treated silica was pressed between thin aluminum foils to form ∅ 5 mm silica wafer. Air was used as a background peak for quantitative FTIR analysis. The relative chemisorbed amount of silane was evaluated by the peak area under the C-H stretching (2885-2973 cm^{-1}) compared to that of internal standard peak (1867 cm^{-1}).

b) Characterization of the Physisorbed Silane. The supernatant solution containing the physisorbed silane in a certain volume of THF 5 mL (HPLC grade), was filtered through poly(tetrafluoroethylene) membrane, pore size 0.22 micrometer, before running SEC analysis. The obtained chromatogram was analyzed for the relative physisorbed amount of silane by the total peak area of each silane species, monomer to oligomer.