

CHAPTER IV

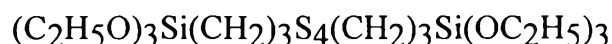
RESULTS AND DISCUSSION

Chemical modification of the silica surface by silane Si-69 has been studied to increase the interaction between inorganic silica and organic rubber. Hence, the present study is on the viewpoint to improve the composite properties by considering the effect of media polarity and silane concentration on the chemisorption and physisorption of silane onto silica. The chemisorption was analyzed by quantitative FTIR technique and the physisorption was investigated by SEC technique.

4.1 FTIR Analysis

The FTIR spectra were observed by making the silica wafer which has the advantages such as simple sample preparation, providing very clear and thin film, and obtaining higher sample concentration than the KBr pellet method.

Figure 4.1 shows the FTIR spectra of the untreated fumed silica, silane Si-69 and the treated silica. The formulation of Si-69 is shown below which generates the C-H stretching at 2885-2973 cm^{-1} .



The structure of fumed silica is SiO_2 with the silanol groups at the silica surface, thus, the sharp free silanol and the broad hydrogen bonded silanol peaks at 3744 and 3500 cm^{-1} , are observed, respectively. The combination

band of siloxane bond can be seen at 1867 cm^{-1} . The band below 1400 cm^{-1} is an overabsorption resulting from the large amount of siloxane bonds in silica particles by the wafer technique.

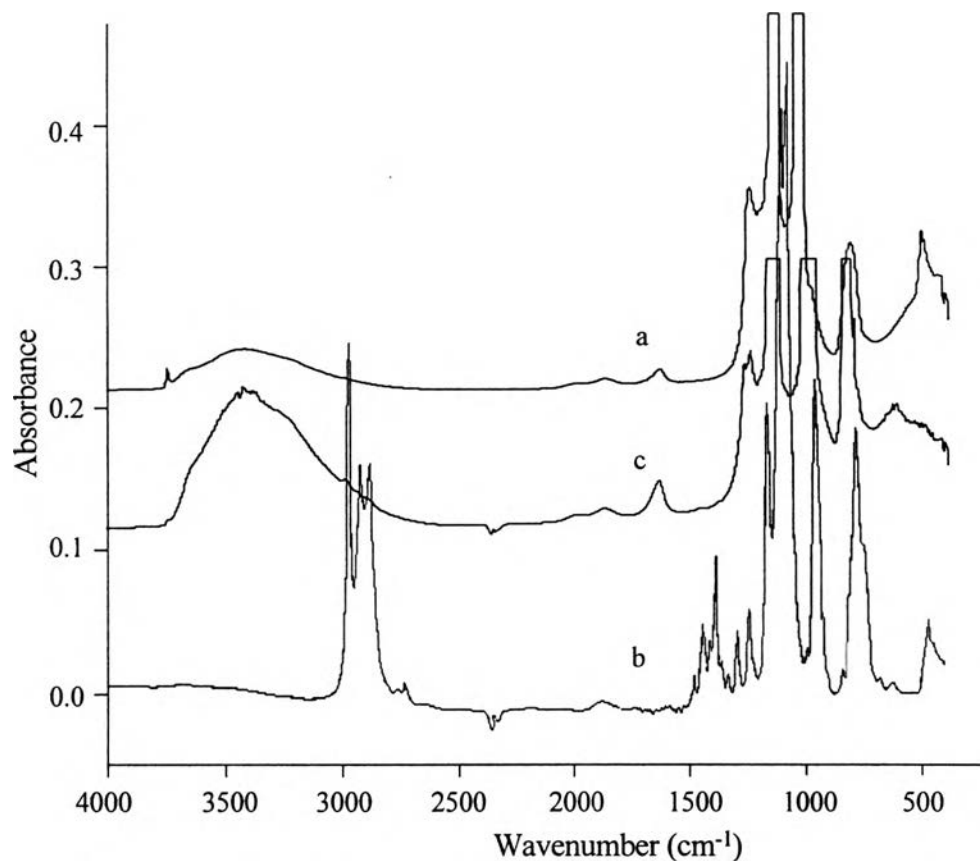


Figure 4.1 FTIR spectra (a) untreated silica; (b) silane Si-69; (c) treated silica.

FTIR (Wafer, cm^{-1}) :- 3744 (free O-H), 3500 (hydrogen bonded O-H), 2885-2973 (C-H stretching),
1867 (combination band)

Comparing silica and Si-69, the untreated silica does not show C-H stretching band. Therefore, it is clarified that silane treated silica has both less

intensity of free silanol band and C-H stretching band which are not presented in the untreated silica spectrum (Figure 4.1). The C-H stretching band is chosen to be the characteristic peak for quantitative FTIR analysis to find the relative amount of chemisorbed silane. The combination band is selected to be the internal standard band to eliminate the effect from sample weight or thickness variation for quantitative FTIR analysis.

The relative chemisorbed amount of silane can be calculated by the following equation:

$$\text{Relative amount of chemisorbed silane} = \frac{\text{Area under C - H stretching band}}{\text{Area under combination band}}$$

Area under C-H stretching band can be calculated after applying the baseline correction following by the integration of area under that peak (Figure 4.2). Area under combination band can be achieved by the spectral curve fitting from small composition peaks and simulating the small peaks as the components of the original peak (Figure 4.3). The actual area is calculated by the integration of the individual combination band.

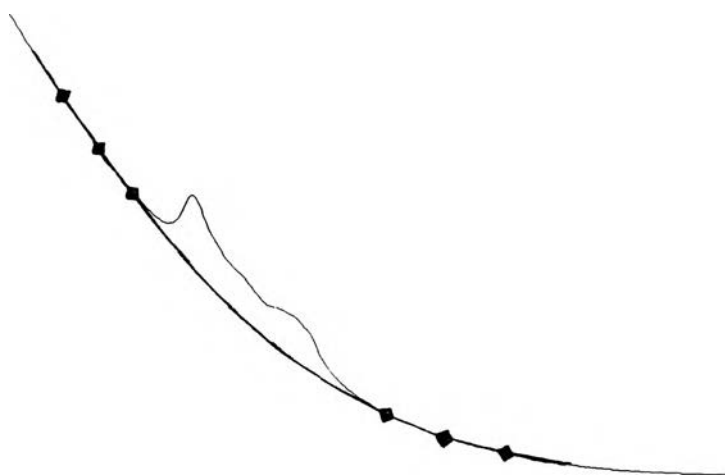


Figure 4.2 Baseline correction of the C-H stretching band.

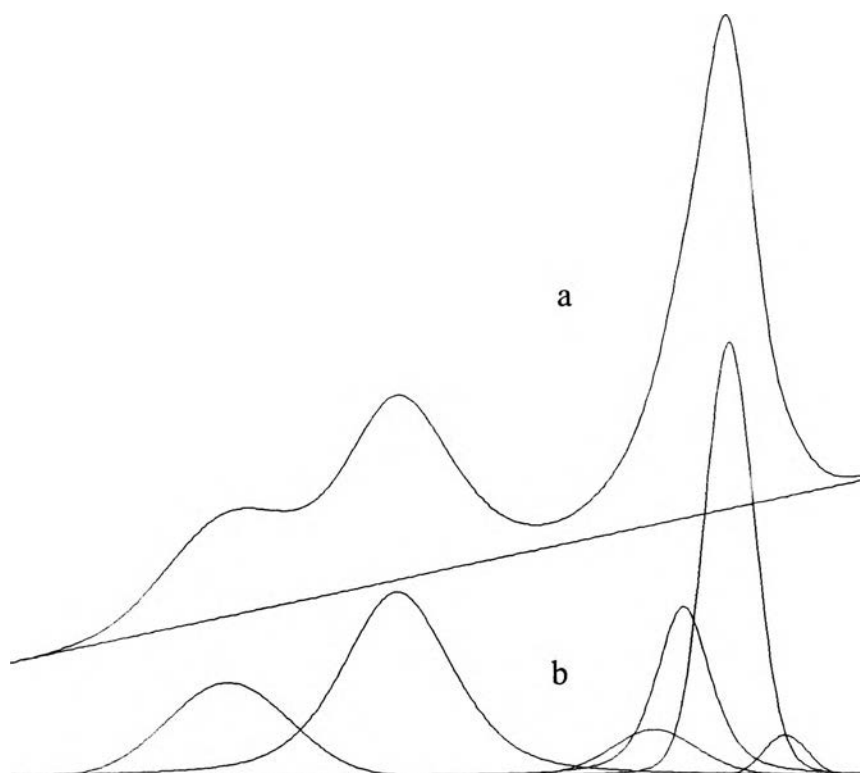


Figure 4.3 Spectral curve fitting of the combination band (a) the obtained peak; (b) each peak component after curve fitting.

4.2 Media Polarity Effect

In this study, we focus on the effect of polar and nonpolar media on the adsorption behavior of the silane coupling agent onto silica and the efficiency of the adsorption. Polarity of the media was varied from the solubility parameter. Five media (ethanol, isopropanol, dioxane, benzene, and hexane) were used comparing to that of water media. Except the case of water media, all studies were done in non aqueous media to avoid the hydrolysis reaction by water and other related factors that may influence the media polarity effect study.

4.2.1 Chemisorbed Silane in Polar and Nonpolar Media

The effect of media polarity on the relative amount of chemisorbed silane is summarized in Figure 4.4. The graph reveals that the significant relative chemisorbed amount was achieved in the high polar media system, especially water. The amount of chemisorbed silane was found to decrease in the nonpolar media system. However, it should be noted that the moderate polar media system gives the least amount of chemisorbed silane.

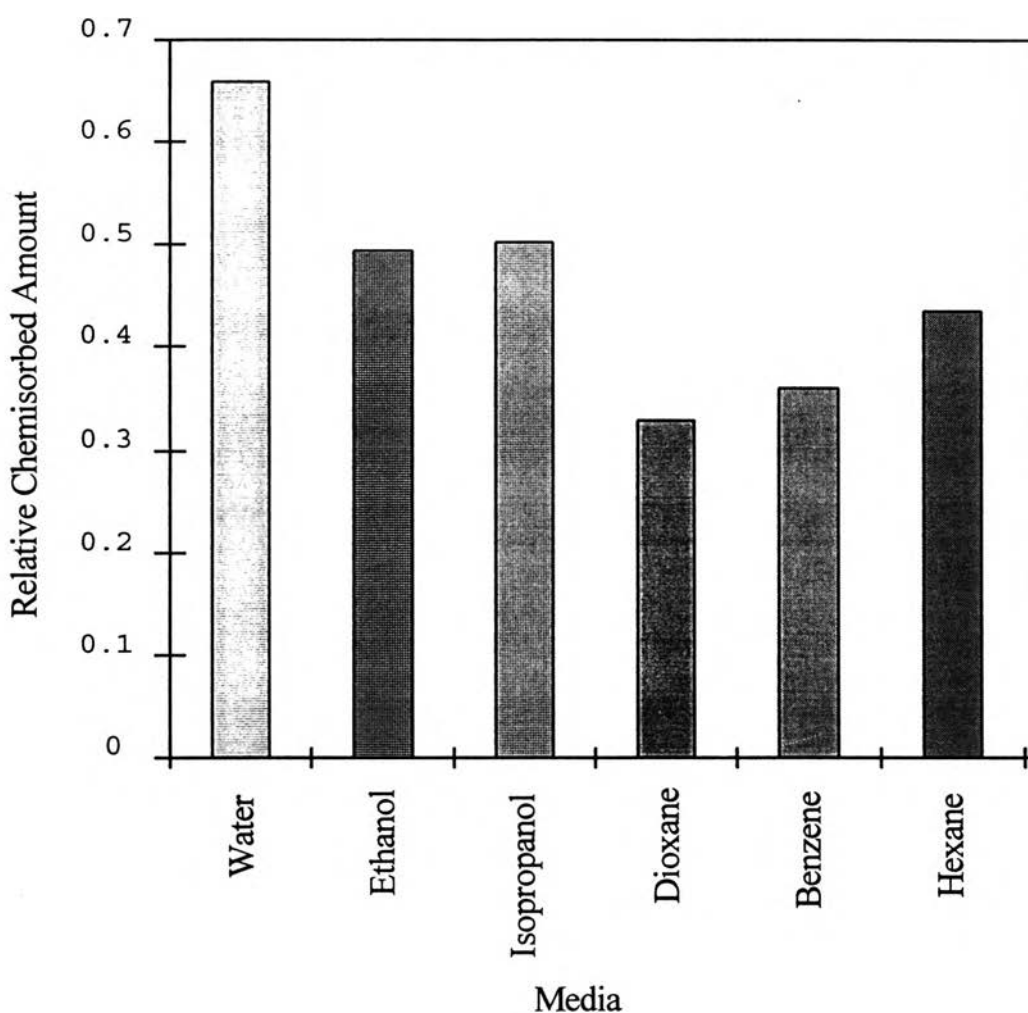


Figure 4.4 Effect of media polarity on the relative amount of chemisorbed silane.

Comparing water to the high polar media, represented by ethanol, though the solubility of silane in water is worse than that in ethanol media, silane can be hydrolyzed efficiently by water. This results in a large amount of active silane hydrolyzate which can be condensed further onto the silica surface. As a result, it provides the high probability of silane condensation onto silica surface and induces the large amount of chemisorbed silane. However, in ethanol, silane is known to be more soluble in alcohol than in water. Thus, the silane tries to dissolve in the solvent than to adsorb onto the silica surface. Furthermore, the hydrolysis of silane occurs incompletely by the trace amount of water in the media and/or by the water molecule on the silica surface. Thus, the condensation on silica surface is controlled by the amount of silane hydrolyzate. As a result, the less chemisorbed amount is formed in the alcohol than that in water.

In order to study the media effect in non-aqueous system, silane concentration was controlled to be as low as 0.1 layer equivalent. In this case, silane hydrolyzate will predominantly react with silica rather than react with each other to form higher molecular weight oligomers, thus, the high molecular weight of chemisorbed silane can be excluded.

However, if water is not taken into consideration, Figure 4.4 shows that alcohol gives higher chemisorbed amount than that of nonpolar media as seen in the case of ethanol, isopropanol, dioxane, benzene, and hexane. It is known that in polar media, silane is more hydrolyzed by the trace amount of water in the media and/or on the silica surface than in nonpolar media. In polar media, silica is well dispersed, which provides an effective surface area for silane to couple onto silica.

However, in nonpolar media such as hexane the condition is slightly different. Silane in nonpolar system is difficult to be hydrolyzed by the trace amount of water in the media owing to the phase separation between the

water and nonpolar media. It is known that the hydrolysis of silane can be achieved by the trace amount of water on silica surface. Here, it can be mentioned that silane is hydrolyzed mainly by the trace amount of water on silica surface. As a result, there is less amount of silane hydrolyzates to form chemisorption in the system. Moreover, in nonpolar system, silica prefers to form hydrogen bond to each other through the silanol groups and acts as a micelle which limits the surface area for chemisorption. Small amount of water on the surface further enhances bridging effect by hydrogen bond formation with the surface silanols. This can be concluded as shown in Figure 4.5.

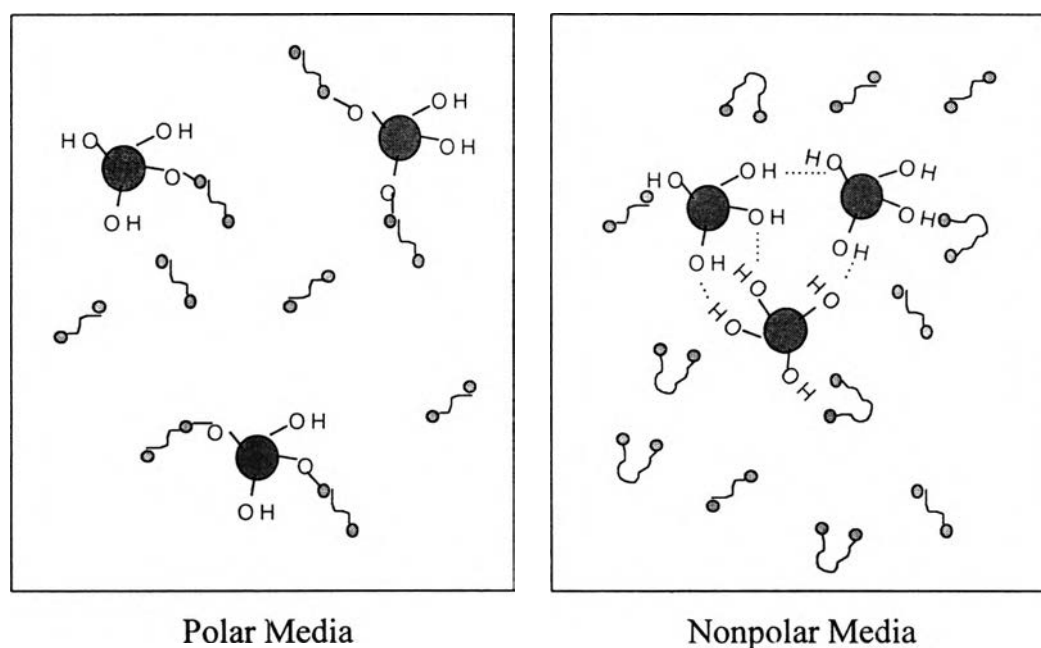


Figure 4.5 Proposed model for silane treatment in polar (ethanol, isopropanol) and nonpolar media (dioxane, benzene, and hexane) systems.

4.2.2 Physisorbed Silane in Polar and Nonpolar Media

Physisorbed silane can be extracted quantitatively after treated silica was washed thoroughly with THF, Ishida *et al.* (1984) indicated that

physisorbed silane will be formed as a monomer to some oligomers. A representative of physisorbed silane analyzed by SEC can be shown as Figure 4.6. The chromatogram consists of many species such as monomer, dimer, trimer, and so on. The molecular weight of each species based on the polystyrene standard can be calculated from the retention time of that species. The relative amount of physisorbed silane is determined by total area under each peak.

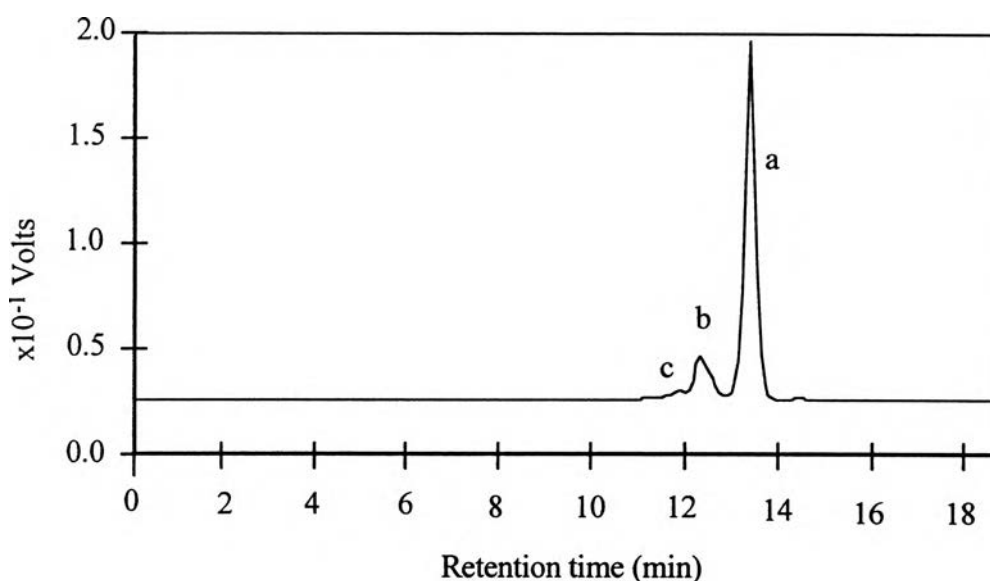


Figure 4.6 SEC chromatogram of the physisorbed silane (a) monomer; (b) dimer; (c) higher molecular weight species.

As shown in Figure 4.7, comparing the alcohol to nonpolar media, the result reveals that nonpolar media induced higher physisorption than polar media. In alcohol, most silane is hydrolyzed and forms as a chemisorbed species on silica, while the small amount of silane will form hydrogen bonding with chemisorbed silane to be physisorbed silane. However, in nonpolar media, only small amount of silane is hydrolyzed and forms as a chemisorbed silane

(as discussed in 4.2.1). As a result, the most part of silane forms the hydrogen bonding to each other to be physisorbed silane.

It should be noted that water is an exceptional case. Water media provides the highest chemisorbed silane owing to the high amount of silane hydrolyzates as discussed in 4.2.1. Here, as shown in Figure 4.7, water also shows high physisorption. This can be explained that some amount of silane hydrolyzates in water media also react with each other to be other oligomer species and remained in the system as a physisorbed silane.

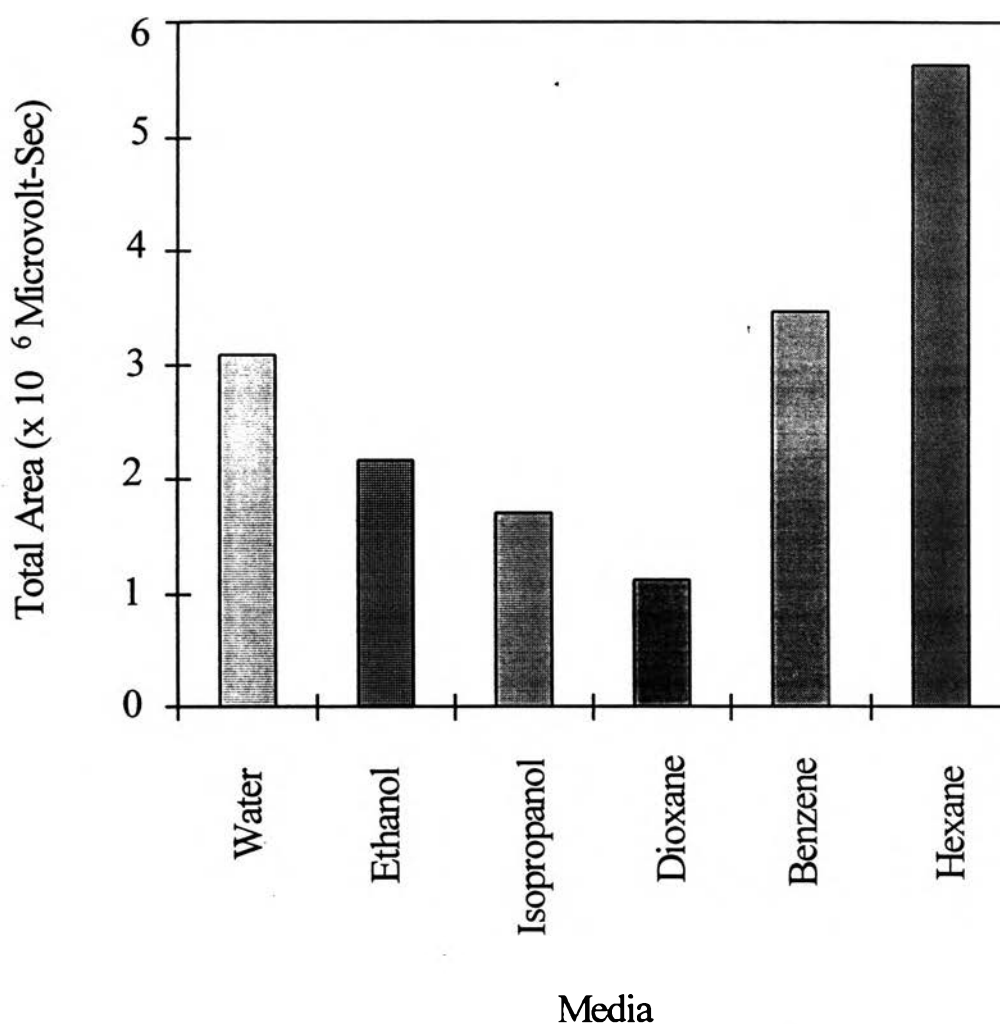


Figure 4.7 Relative physisorbed amount of silane as a function of silane concentration in various media.

From the media polarity effect study, we can conclude that in the polar media, the chemisorption is dominant while in the nonpolar media, the physisorption is dominant. Therefore, the polar media is more appropriate for silane treatment than the nonpolar media due to the higher chemisorption and lower physisorption of silane.

4.3 Silane Concentration Effect

In the present work, the concentration of silane was varied from 0.005 monolayer to 3 layers to study the silane concentration effect on the chemisorption and physisorption of silane onto silica surface. Ethanol representing for the polar media and hexane representing for the nonpolar media, was used to investigate the silane concentration effect in polar and nonpolar condition.

4.3.1 Chemisorption Analysis

Figure 4.8 demonstrates the relative chemisorbed amount of silane as a function of silane concentration in ethanol and hexane media system. The plot reveals that ethanol media gives higher chemisorbed amount than hexane media which is in agreement with the previous media polarity effect study (see 4.2.1). In both media systems, in which the silane concentration increases, there is an increase in the relative amount of chemisorbed silane until the saturation point of chemisorption. After the saturation point, at higher silane concentration, the relative chemisorbed amount is fluctuated because silane will be condensed with each other to form dimer, trimer, and so on. The high molecular weight species are more difficult to come close to silica surface and

align themselves to couple onto silica surface. This evidence can be clarified by Figure 4.9 and 4.10.

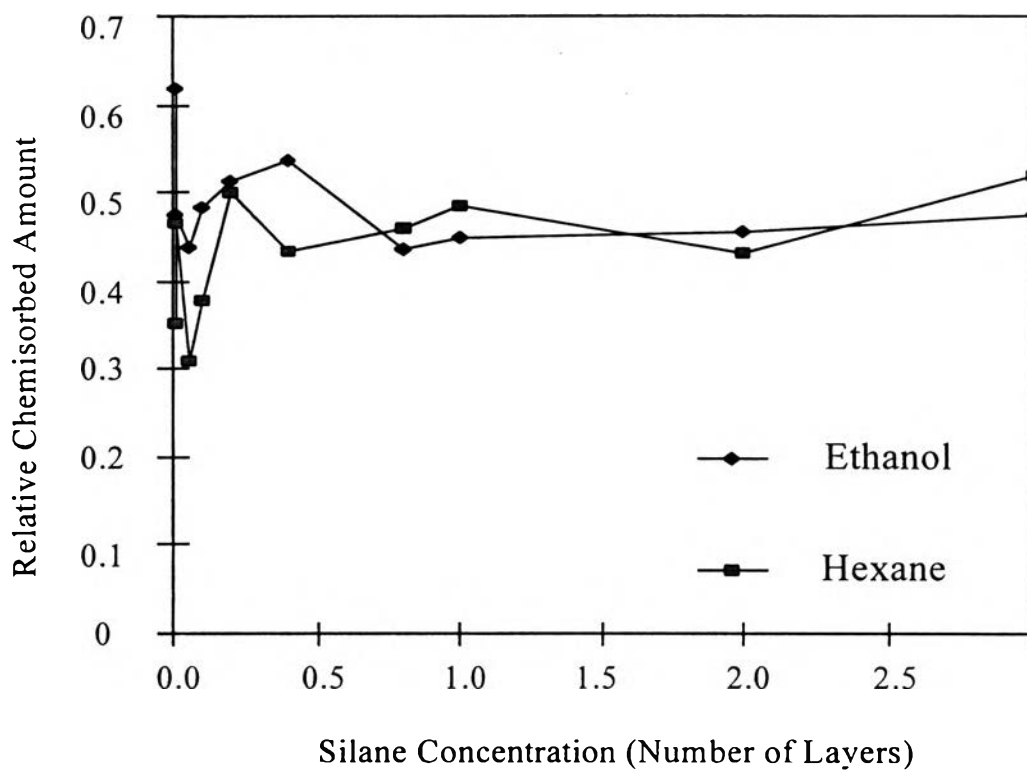


Figure 4.8 Silane concentration effect on the relative chemisorbed amount of silane in ethanol and hexane media systems.

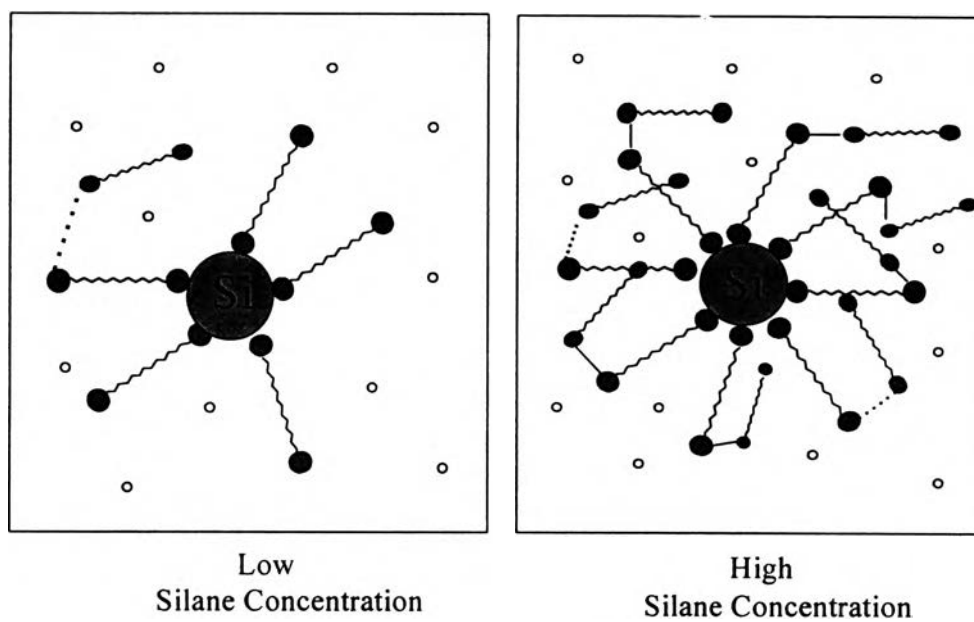


Figure 4.9 Proposed model for silane concentration effect in polar media.

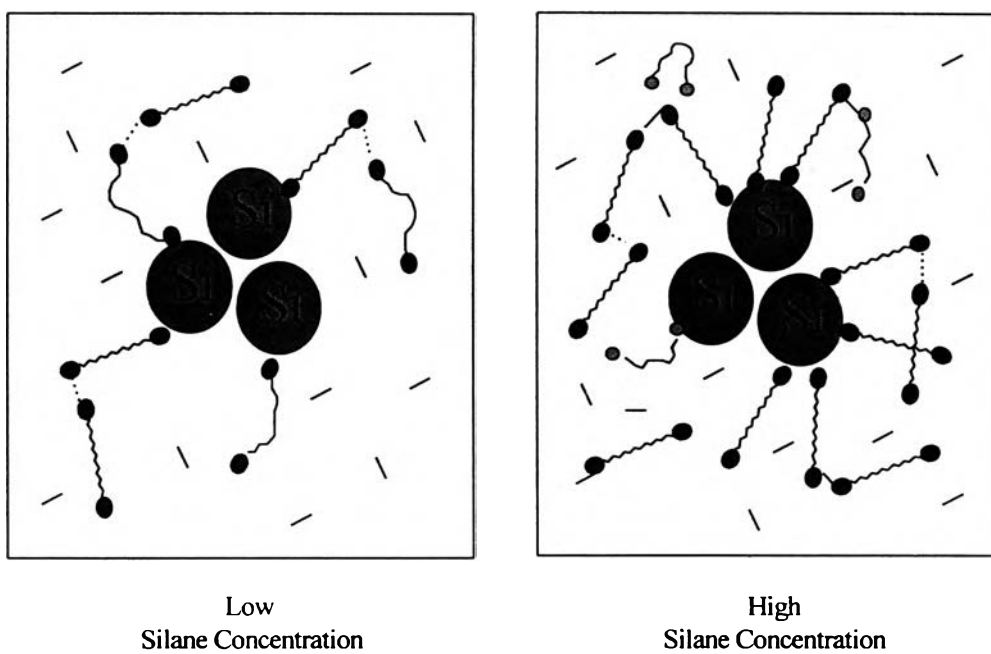


Figure 4.10 Proposed model for silane concentration effect in nonpolar media.

This result agrees with the previous study of Nishiyama *et al.* (1991) for γ -MPS silane treatment onto colloidal silica. It is reported that the amount of chemisorbed silane increases with silane concentration until the concentration reach 33.0 mg/ml which is the maximum amount of silane on the silica surface corresponding to 2.3 silane molecules chemisorbed on 1 nm² of silica surface.

Another attention from Figure 4.8 is that the saturation point of chemisorbed silane in ethanol media is faster than that in hexane media system (at silane concentration 0.4 monolayer for ethanol media and 1 monolayer for hexane media). This is because the polar media system produces mostly chemisorption while the nonpolar media induces mostly physisorption as the previous media polarity study. As a result, it is necessary to add more silane molecules to form chemisorption and achieve the saturation point. From this reason, the polar media system gives the chemisorbed saturation point at lower silane concentration than the nonpolar media system (Figure 4.11).

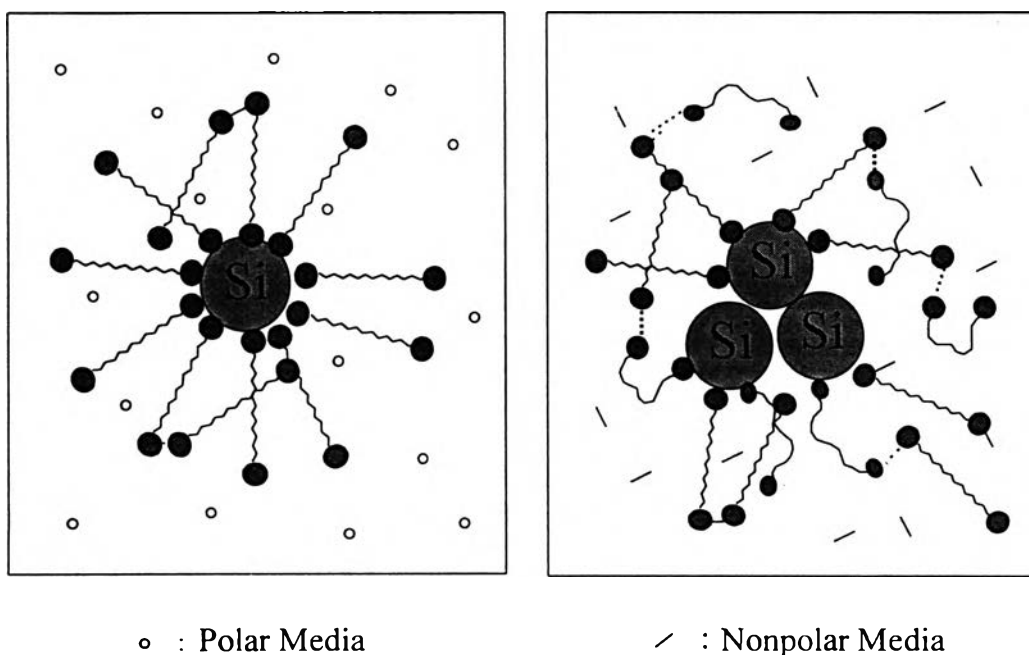


Figure 4.11 Proposed model for saturation point of chemisorbed silane in polar and nonpolar media systems.

4.3.2 Physisorption Analysis

Figure 4.12 shows the relative amount of physisorbed silane as a function of silane concentration in ethanol and hexane media systems. Hexane medium gives more physisorption than ethanol medium due to the physisorption dominant in hexane media system. In both media, the higher silane concentration, the more physisorbed amount of silane in the system. This may be due to the fact that the more silane concentration, the higher probability of silane to form the hydrogen bond with the chemisorbed silane or with the silica surface.

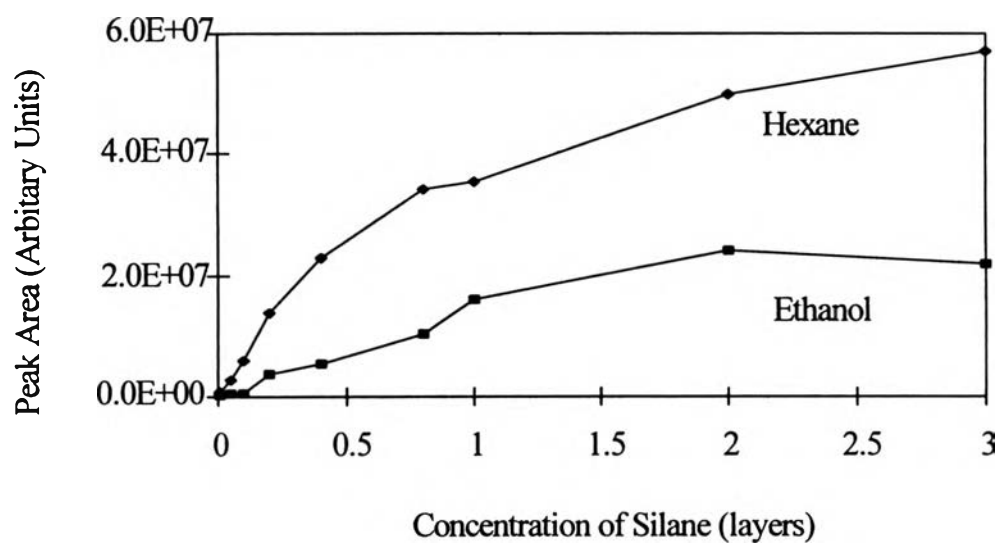


Figure 4.12 Relative amount of physisorbed silane as a function of silane concentration in ethanol and hexane media systems.