# CHAPTER IV

RESULTS AND DISCUSSION

## 4.1 Silica Content Effects on Viscosity Behavior of MMA/Silica Composite

Kawaguchi et al. reported that integral blend of the homogeneous fumed silica suspensions with various silica content can be prepared by mechanical mixing and shaking (Kawaguchi et al., 1997) with coupling agent. In the present work, the integral blend of MMA/Silica was prepared by stirring in the glassware to avoid the impurity particles from milling ball. γ-MPS was applied as a coupling agent and was added gradually with the partial amount of silica till the mixture achieved the required content. Ishida et al. reported that when the silane coupling agent reacts with silica, the viscosity will be decreased (Ishida et al., UK patent 2,213,824). Here, the viscosity of the mixture was studied as a function of time. When the time for stirring increased, the viscosity of the solution decreased and became constant at equilibrium state, as shown in Figure 4.1.

The decrease of viscosity can be mentioned as a result of the breakdown of aggregates. Since some small aggregates are usually present in the fumed silicas, breakdown of such aggregates by the mixing and reaction of silane onto silica surface will affect directly the viscosity. The equilibrium state was achieved with optimum adsorption of silane onto silica. Figure 4.2 shows the viscosity at equilibrium state of each % silica systems. It was found that the viscosity at equilibrium state increases without linear function of the silica constant and increases significantly at higher silica content.
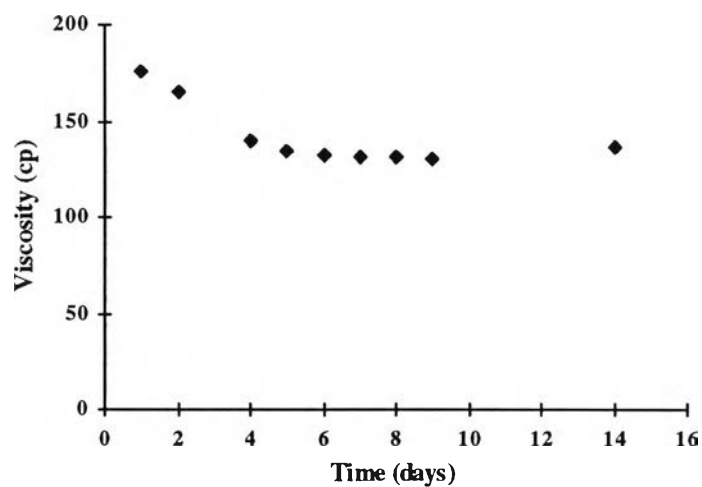
Figure 4.1 Viscosity of 30% silica with a monolayer equivalence
of silane coupling agent as a function of time.
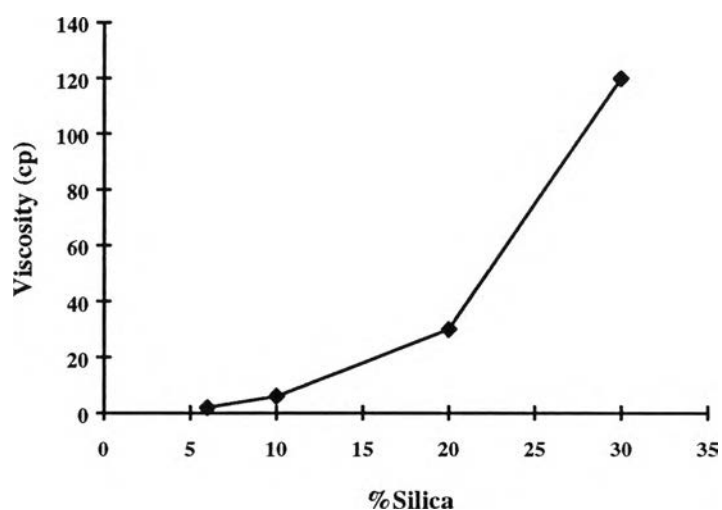
Figure 4.2 Viscosity at equilibrium state of various % silica systems
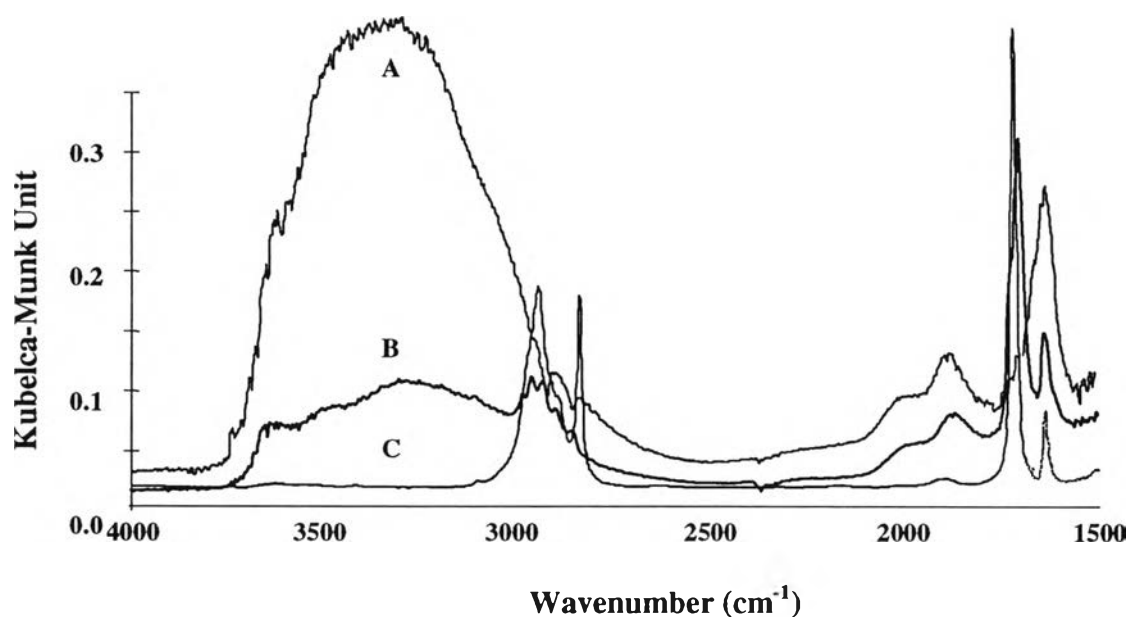for a monolayer equivalence of silane coupling agent.

Figure 4.2 shows that in low silica content at equilibrium state, the silica particles can disperse well in MMA solution and the formation of aggregation is not significant. Thus, the viscosity at equilibrium of such system is low. Increasing of silica content results in increasing size of silica aggregates. As a result, the viscosity at equilibrium state is high.

4.2 Silica Content Effects on Adsorption Behavior of MMA/Silica Composite

In integral blend treatment, it is known that the silane molecules are hydrolyzed by the trace of water on the silica surface and condensed immediately with the silanol group (Si-OH) on the silica surface to form siloxane bond (Si-O-Si) (Ishida, 1993). Some of hydrolyzed silane may form either oligomers or high molecular weight polysiloxanes, depending only on initial reaction conditions, then, adsorbed physically onto silica surface. Because there are numerous species of physisorbed silane, such as, monomer, dimer, trimer and other oligomers, which are known to be similar in the structure. Thus, size exclusion chromatography is a useful tool to analyze physisorbed silane.

Normally, physisorbed silane can be washed out easily by THF owing to the similarity in solubility parameter. The difference in retention time corresponds to the difference in molecular weight of physisorbed silane. The relative total amount of physisorbed silane was evaluated from the integration under each peak from SEC chromatogram that represented the physisorbed silane species. The amount of unreacted silane can be evaluated by the same way of physisorbed silane. The diffuse reflectance technique has substantially advanced the ability to study the chemistry of adsorbate molecules (Ishida, 1984). Usually, scattering changes are small within a limited spectral range so

that conversion of a diffuse reflectance spectrum by the Kubelca-Munk function gives a plot which is scaled linear in concentration and thus directly comparable to an absorbance spectrum.


Figure 4.3 DRIFT spectra of γ-MPS treated fumed silica of 20% silica

system with a monolayer equivalence of silane at 5 days

(A) fumed silica; (B) γ-MPS treated fumed silica; (C) γ-MPS.

Figure 4.3 illustrates the spectra obtained from the diffuse reflectance experiment. Spectrum A is the fumed silica in mid-IR region from 4000-1500 cm^{-1}, spectrum B is the γ-MPS treated fumed silica and spectrum C is the γ-MPS.

From spectrum B, the species on surface of fumed silica are shown by the C-H stretching mode at 3000-2800 cm^{-1}, the C=O band at 1720 cm^{-1} and the C=C band at 1638 cm^{-1}. The C=O band in γ-MPS has a large specific absorptivity, allowing for high-sensitivity measurements. The C=O band of γ-MPS on silica appears at 1710 cm^{-1} due to hydrogen bonding. Hence, it is

clarified that γ-MPS is adsorbed onto the silica. The band at 1867 cm^{-1}, which is likely a combination band, was used as the internal standard band to determine the amount of silica. The infrared bands of γ-MPS are linear in intensity or area under peak with concentration of the γ-MPS (Miller and Ishida, 1986). Thus, the characteristic peaks of C=O bands can be applied for quantitative analysis using combination band as an internal standard band.
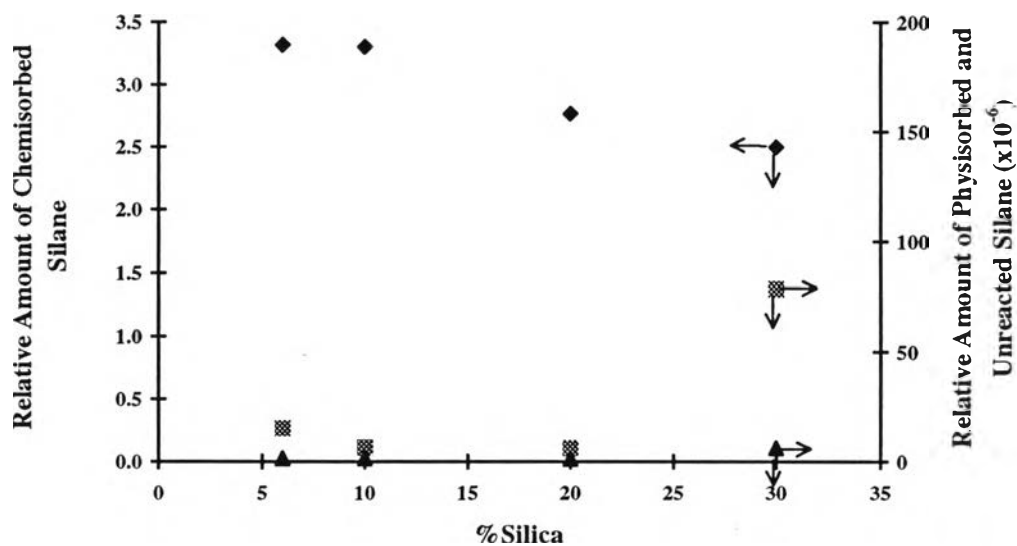
Figure 4.4 Amount of γ-MPS unreacted, physisorbed and chemisorbed on silica surface as a function of silica content with a mono-layer equivalence of silane at 8 days ◆ chemisorbed silane; ■ physisorbed silane; ▲ unreacted silane.

Figure 4.4 demonstrates the relative amount of unreacted, physisorbed silane and chemisorbed silane as a function of silica content with a monolayer equivalence of silane at 8 days. As shown in Figure 4.4, in the case of chemisorption, it is found that when the silica content is higher (20%, 30%), the chemisorbed silane is lower. It should be noted that in all cases of silica content, monolayer equivalence of silane was added into the system and is expected to form the similar adsorption level. However, the result reveals that the coupling reaction onto silica to form as a chemisorbed silane becomes less efficient when the silica content is high. Refering to the viscosity study (see 4.1), at monolayer equivalence of silane, when the silica content is high the viscosity at equilibrium state is high. It can be concluded that silica in high concentration forms aggregates limiting the silane to couple onto silica surface. As a result, the chemisorbed silane for higher silica content is lower than that for low silica content.

In the case of physisorption, the physisorbed silane is derived from monomer, oligomer and high molecular weight of polysiloxane. As shown in Figure 4.4, the total relative amount of all physisorbed silane increases with silica content, while the relative amount of chemisorbed silane decreases. Since the silane concentration is controlled at monolayer equivalence, the obtained physisorbed silane is mainly related to the silane amount of which can not form as a chemisorbed silane. Therefore, the physisorbed silane is dominant in high concentration of the silica. This can be summarized as a schematic diagram as shown in Figure 4.5.
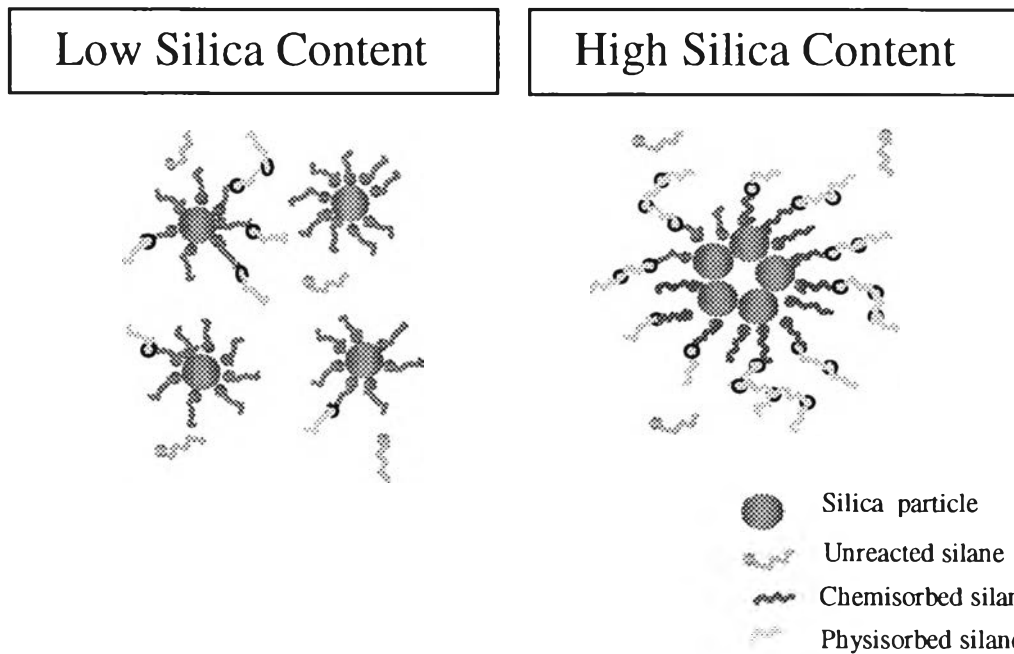
Figure 4.5 Model for physisorption and chemisorption effected from silica content with a monolayer equivalence of silane.

The translucent appearance can be observed by the appearance of the mixture. It should be noted that when the silica content increases, the transparency will be increased. Refering to the relationship of silica and adsorption behavior, it can be said that high physisorbed silane is directly related to the transparency of the mixture. In other words, the translucent appearance of the PMMA/Silica composite can be achieved by the increment of physisorbed silane.

From this part of experiment, 6 % silica system was taken as a condition to study the effect of silane concentration. This system was chosen because high content of chemisorbed silane in the system.

4.3 Silane Concentration Effects on Viscosity Behavior of MMA/Silica Composite

The time for achieving constant viscosity was studied by varying the concentration of silane from 0.2 to a monolayer equivalence. A monolayer equivalence of silane in MMA solution is defined as a layer of silane molecules that is necessary to form a layer under the ideal condition. Figure 4.6 shows the result when the silica content is maintained at 6% and achieves the constant viscosity. It should be noted that the viscosity of the silica suspension at each silane concentration is almost the same for 0.4-1.0 layers range (approximately 0.0015 Pa.s.) and raises up to be 0.048 Pa.s for 0.2 layer.
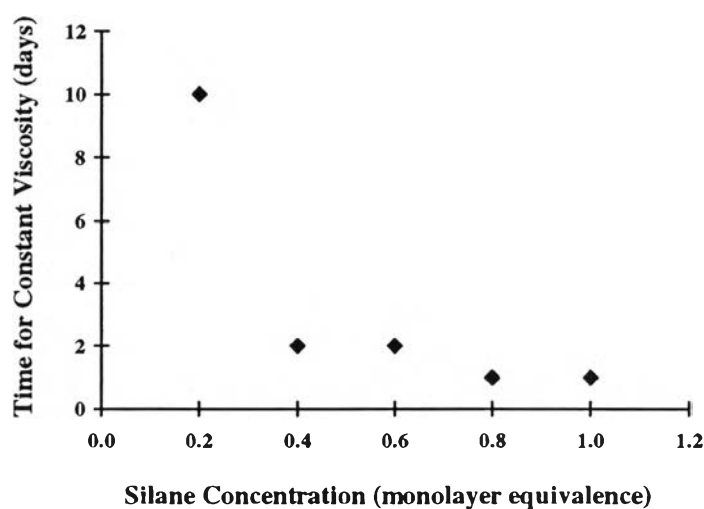
Figure 4.6 Reaction time for achieving constant viscosity for each silane concentration in the case of 6% silica.

It was found that when the silane concentration becomes low, the time to achieve the constant viscosity is longer than in the case of high silane concentration. It can be said that in low silane concentration, there is a small amount of reactive silane that couples onto silica surface, thus, this system requires a long time for constant viscosity. In the case of high silane concentration system, there is a large amount of silane molecules that is ready to adsorb on silica surface and the equilibrium structure is reached at very early stage of treatment.
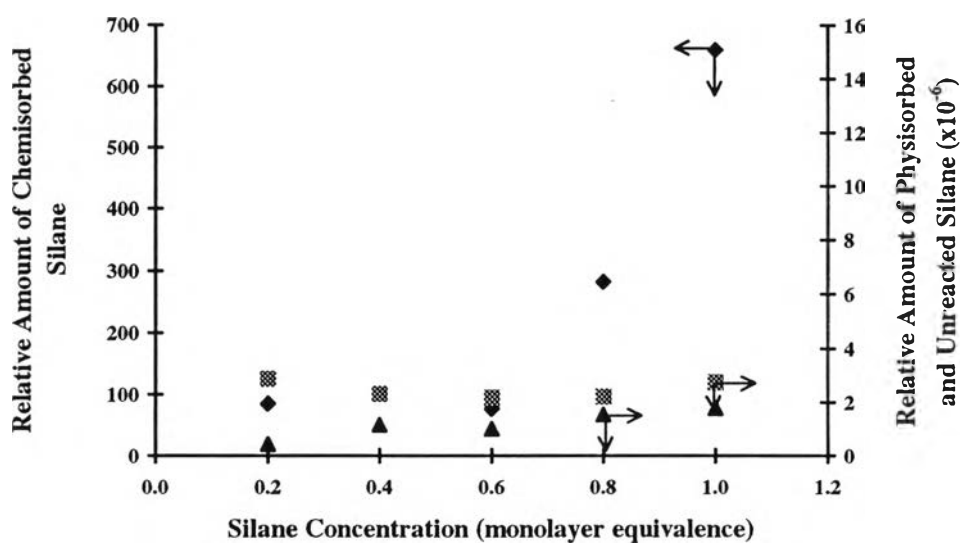
The concentration of silane in MMA solution is defined as a layer of silane molecule that can cover all silica surface (a monolayer equivalence by theoretical value). The concentration range from 0.2 layers to a monolayer equivalence of γ-MPS was applied for the study. Figure 4.6 shows that the mixture at low silane concentration takes longer time to achieve the constant viscosity.

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4.4 Silane Concentration Effects on the Adsorption Behavior of MMA/ Silica Composite

The adsorption behavior of γ-MPS on silica surface was indicated by Figure 4.7. The chemisorbed silane amount corresponds directly to the silane concentration. In section 4.3, it is found that when the silane concentration is maintained at a monolayer equivalence, in low silica content system, the silane

molecules have high potential to form covalent bond with silica surface, then, almost silane molecules are chemisorbed silane and has no effect on physisorbed and unreacted silane. In the present study, silica content is maintained at 6% and the silane concentration is varied from 0.2 to a monolayer equivalence. As shown in Figure 4.7, it is found that when silane concentration is raised to 0.8 layer, the chemisorption increases significantly. The result also reveals that in low silica content, silane is coupled onto silica surface and formed as a chemisorption predominantly while the physisorption maintains in a certain level. As a result, comparing to the changing of chemisorbed silane, the unreacted and physisorbed silane amount can be mentioned as a constant value for all silane concentration.

Figure 4.7 Amount of silane adsorbed on fumed silica as a function of

the concentration of silane in the treatment solution

◆ chemisorbed silane; ■ physisorbed silane; ▲ unreacted silane.

4.5 Silane Concentration Effects on Dynamic Mechanical Properties of PMMA/Silica Composite

In order to study the formation of the interpenetration network by the silane coupling agent with MMA, MMA in 6% silica with variation of silane layer was cured to obtain a sample sheet. The obtained sample sheet was prepared for testing the rheological properties in the temperature mode. It is well known that the dynamic mechanical measurements can be utilized to study dynamic mechanical characteristics of polymeric materials on the molecular level (Eckstein, 1988).

Figure 4.8 shows the rheological properties of MMA-silica composite in damping mode with various silane concentrations. The pure PMMA specimen shows the α transition at 108 $^\circ$C which corresponds to the T_g of PMMA. However, a small increase of T_g can be observed when treated silica has a 0.2 monolayer equivalent coverage of silane. In addition, a drastically increased in T_g for the same level is observed when silane coverage equals to 0.4-0.8 monolayer equivalence. In this case, T_g is shifted to be approximately 112 $^\circ$C.

It is known that the change in T_g is related to the morphology of the composite. In the case of low silane coverage (0.2 monolayer equivalence), the chemisorption of silane onto the silica surface cannot be achieved efficiently which induced the aggregation of silica particles in the composite while high silane coverage (0.4-0.8 monolayer equivalence), silica particles are well separated. For the system with high silane concentration, in contrast to those with low silane concentration, there is a high probability to contribute the interaction between the chains of PMMA and silica treated γ-MPS for hard segment formation, which results in strong interpenetrating network. The shift in T_g for each silane concentration indicates that there is an interpenetrating network related to the silane concentration. The above phenomena implies

that a high concentration of chemisorbed silane is required for a strong interpenetrating network formation of the PMMA/silica composite.
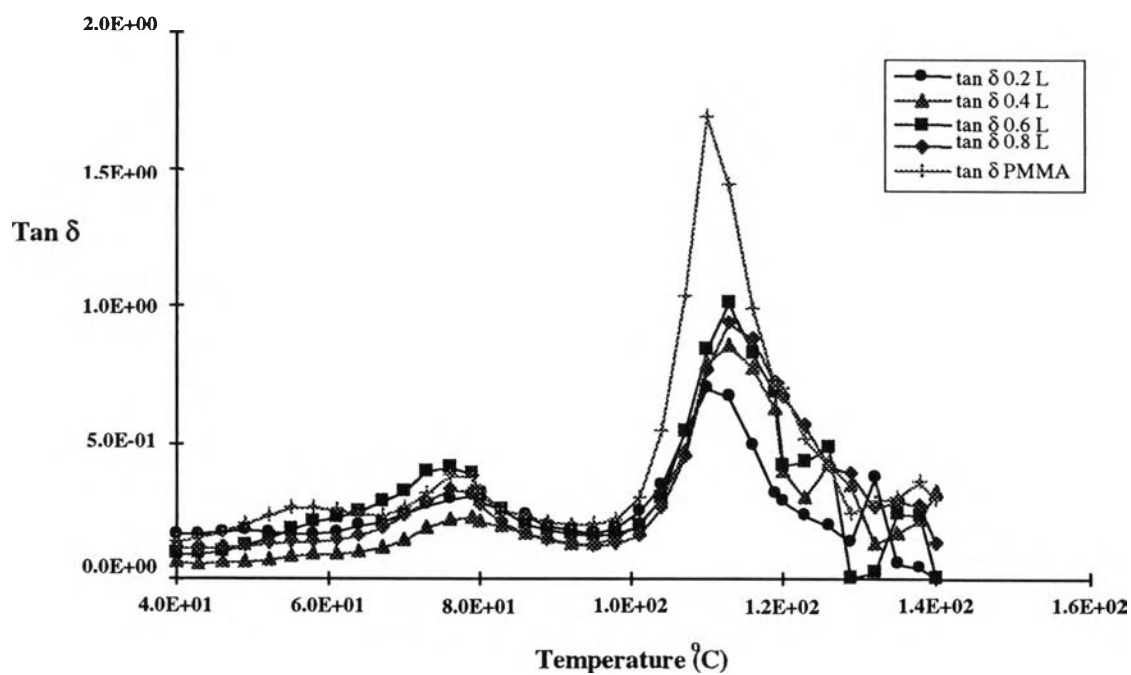
Figure 4.8 Dynamic mechanical properties of treated silica filled MMA composites in various silane concentration for 6% silica.