

CHAPTER III

RESULTS AND DISCUSSION

3.1 Film forming sizing agent

The mixture system consisting of γ -MPS and PVAc was used to model the treating solution which is actually used in the production of glass fiber reinforced unsaturated polyester resin composites.

The structural formulae of PVAc is shown in Figure 3-1.

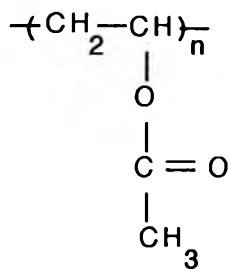


Figure 3-1 Structural formulae of PVAc.

PVAc is expected to influence the silanol condensation of γ -MPS hydrolyzates. There are three possible interactions between PVAc molecules and γ -MPS hydrolyzate. Firstly, the hydrogen bonding between silanol group of γ -MPS hydrolyzate and oxygen atom of carbonyl groups in PVAc.

Secondly, the hydrogen bonding between silanol groups of γ -MPS and oxygen atom of carbonyl groups in other γ -MPS hydrolyzate. Thirdly, the interaction between methacryl-functional groups of γ -MPS and PVAc molecules. From the calculated Hilderbrand solubility parameters of methacryl-functional groups of γ -MPS and PVAc molecules, it was found by Ishida et al. that their solubility parameters are closed to each other. This means that the methacryl groups of γ -MPS and PVAc molecules are miscible. FTIR spectra of the model sizing systems consisting of PVAc at different percent weight are shown in Figure 3-2.

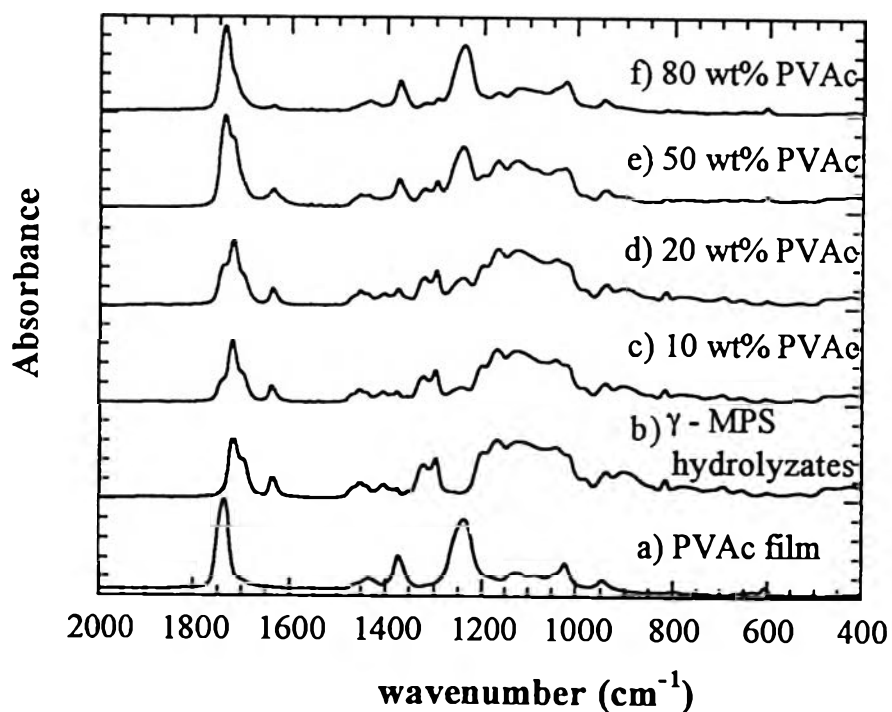


Figure 3-2 FTIR spectra of the model system containing PVAc at different percent weight.

In the γ -MPS hydrolyzate individual system (Figure 3-2b), carbonyl stretching of γ -MPS molecules shows two sharp peaks at 1698 and 1720 cm^{-1} , which refer to hydrogen bonded carbonyl groups and non-hydrogen bonded carbonyl groups respectively. The siloxane band appears in the region 1000 - 1130 cm^{-1} and the Si-O stretching of silanol group appears at 904 cm^{-1} . The 941 cm^{-1} band and 1635 cm^{-1} band derive from the vinyl group of γ -MPS. PVAc film as shown in Figure 3-2a, shows the characteristic carbonyl stretching band at 1737 cm^{-1} which is the carbonyl stretching of PVAc in bulk state. The bands at 1126, 1084 and 1021 cm^{-1} are due to the ester functionality of PVAc. FTIR spectra of the mixture systems containing γ -MPS and PVAc at different % weight are shown in Figure 3-2(c-f). The C=O stretching band of carbonyl groups in the mixture system is more complicated than the system without PVAc because it arises from the overlapped C=O stretching of carbonyl groups in different environments.

The sum of Gaussian and Lorentzian curve fitting method can be applied to resolve the complicated carbonyl bands of the mixture system containing PVAc as shown in Figure 3-3.

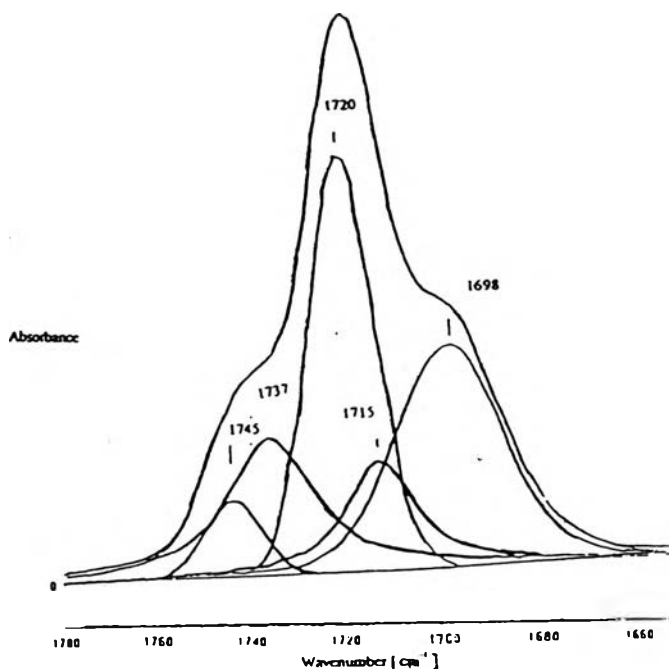
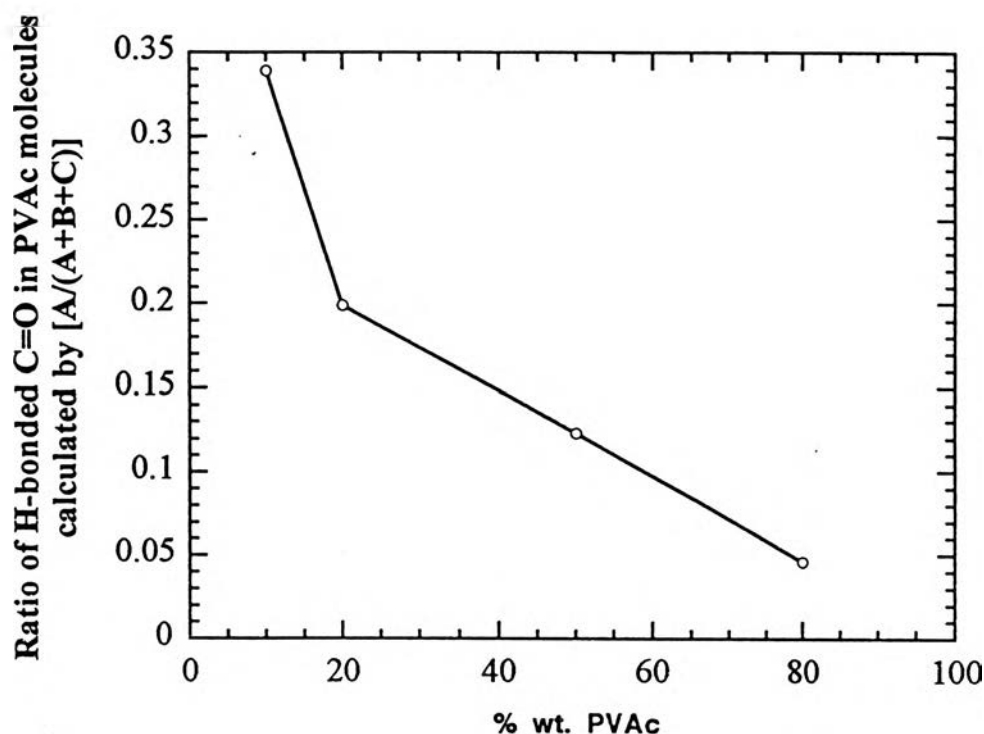


Figure 3-3 The curve fitting for the carbonyl stretching band of model sizing system consisting of PVAc.

The results show 5 individual bands at 1698, 1715, 1720, 1737 and 1745 cm^{-1} . The 1698 and 1720 cm^{-1} bands are the stretching bands of hydrogen bonded and non-hydrogen bonded carbonyl groups of γ -MPS hydrolyzate molecules respectively. The remaining bands come from the C=O stretching of carbonyl groups in PVAc. From these results, it can be concluded that PVAc molecules exist in three states. The first is the PVAc molecules in bulk state which give the C=O stretching band at 1737 cm^{-1} . The second is PVAc molecules which are miscible with the methacryl groups of γ -MPS hydrolyzates which give the C=O stretching band at 1745 cm^{-1} . And the last is PVAc molecules which dissolve in γ -MPS hydrolyzate phase. Carbonyl groups of PVAc molecules of this type form hydrogen bonding with silanol groups of γ -MPS hydrolyzates and give the C=O stretching band at 1715 cm^{-1} .

Figure 3-4 shows the plot of H-bonded carbonyl group of PVAc ratio as a function of % PVAc weight.



A = Absorbance of H-bonded C=O stretching at 1715 cm^{-1} .

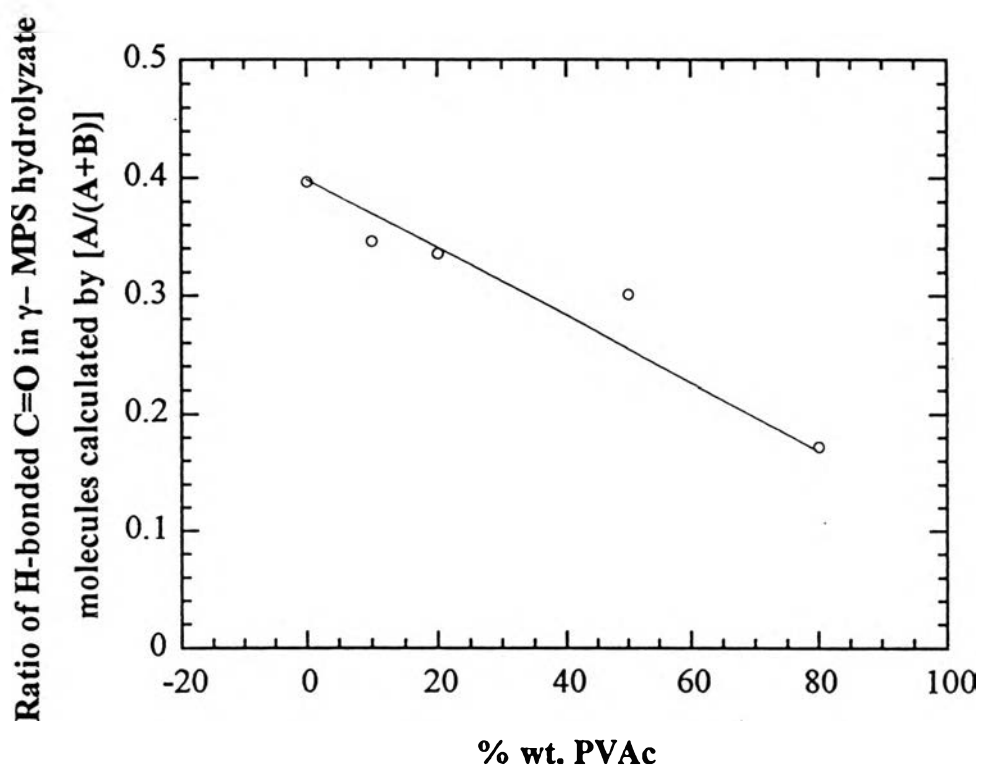
B = Absorbance of free C=O stretching at 1737 cm^{-1} .

C = Absorbance of plasticized C=O stretching at 1745 cm^{-1} .

Figure 3-4 The plot of H-bonded C=O of PVAc ratio as a function of %wt. PVAc.

The reduction of the ratio with increasing % weight of PVAc is observed. It can be concluded that PVAc prefer to exist in the other two states (in bulk state and in interaction with methacryl groups of γ -MPS) rather than to form H-bonding with silanol groups of γ -MPS.

Figure 3-5 shows the plot of H-bonded C=O of γ -MPS molecules ratio as a function of % PVAc weight. The H-bonded C=O ratio in γ -MPS molecules decreased with increasing % weight of PVAc suggesting the molecular diffusion effect of PVAc chains in the systems.



A = Absorbance of H-bonded C=O stretching at 1700 cm^{-1} .

B = Absorbance of free C=O stretching at 1720 cm^{-1} .

Figure 3-5 The plot of H-bonded C=O of γ -MPS molecules ratio as a function of %wt PVAc.

From these results, the morphology of the mixture systems can be postulated as the micelle-like structure in Figure 3-6.

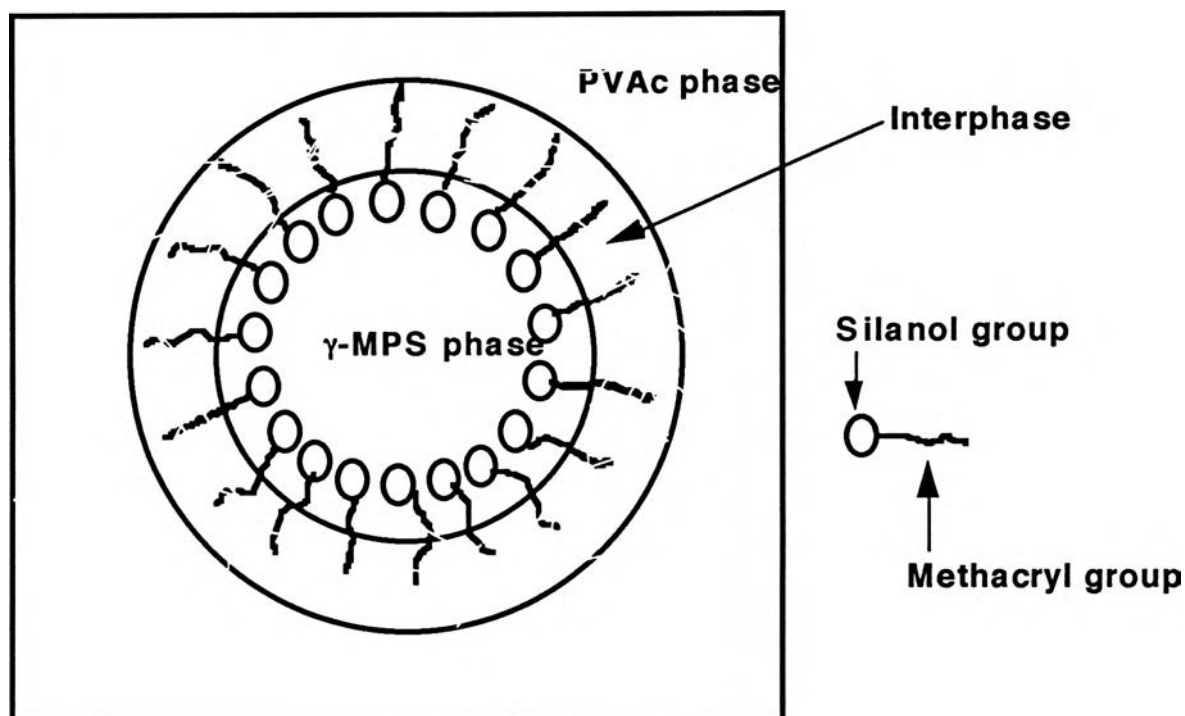


Figure 3-6 The postulated micelle-like structure morphology of the model sizing system containing PVAc.

It can be assumed that there are three phases in the system, namely γ -MPS oligomer phase, PVAc phase, and the interphase which occur from the miscibility of methacryl-functional groups of silane and PVAc molecules. The silanol groups of γ -MPS molecules are the hydrophilic groups and methacryl-functional groups of γ -MPS molecules are hydrophobic groups, thus at the interphase, the γ -MPS molecules have all their silanol groups embedded in the γ -MPS phase with the methacryl-functional groups pointing outwards into the PVAc phase.

The influence of PVAc sizing agent on the silanol condensation of γ -MPS can be considered from the plot between the silanol absorbance at 904 cm^{-1} divided by the vinyl absorbance at 1635 cm^{-1} as a function of % PVAc composition (Figure 3-7).

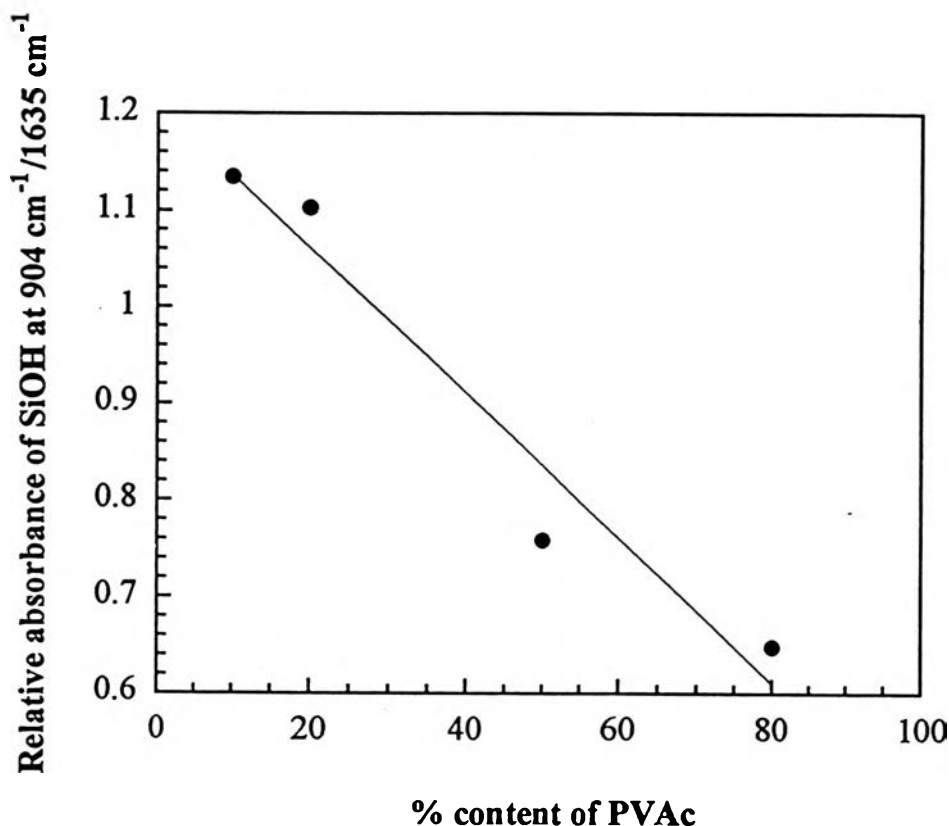


Figure 3-7 The plot of relative absorbance of Si-OH at $904\text{ cm}^{-1}/1635\text{ cm}^{-1}$ as a function of %PVAc contents.

The trend of decreasing in the absorbance of silanol group with increasing % weight of PVAc is observed. It can be implied that the existence of PVAc in the system causes the acceleration in silanol condensation. This result can be used to confirm the postulated micelle-like structure morphology in Figure 3-6. When PVAc molecules are present in the system, they will be miscible with the methacryl groups of γ -MPS, thus the silanol

groups are free to move than the system without PVAc. The encounter between silanol groups can occur easier so the condensation between silanol groups is accelerated when comparing with the system containing no PVAc.

3.2 Lubricating sizing agent

The final structure of silane coupling agent at the interphase of fiber glass reinforced matrix resin composite in the presence of sizing agent system depends greatly on the initial hydrolysis and condensation reaction of the treating solution.

The model system consisting of γ -MPS and PEG at different composition of PEG was used to investigate the condensation of γ -MPS hydrolyzates in the presence of lubricating component by using GPC and FTIR technique.

Figure 3-8 shows the molecular weight evolution of γ -MPS hydrolyzates alone. The chromatogram of this system is broad suggesting the various sizes of oligomers in the system. The increase of molecular weight is stepwise according to drying time. The higher molecular weight oligomers appear at longer drying time.

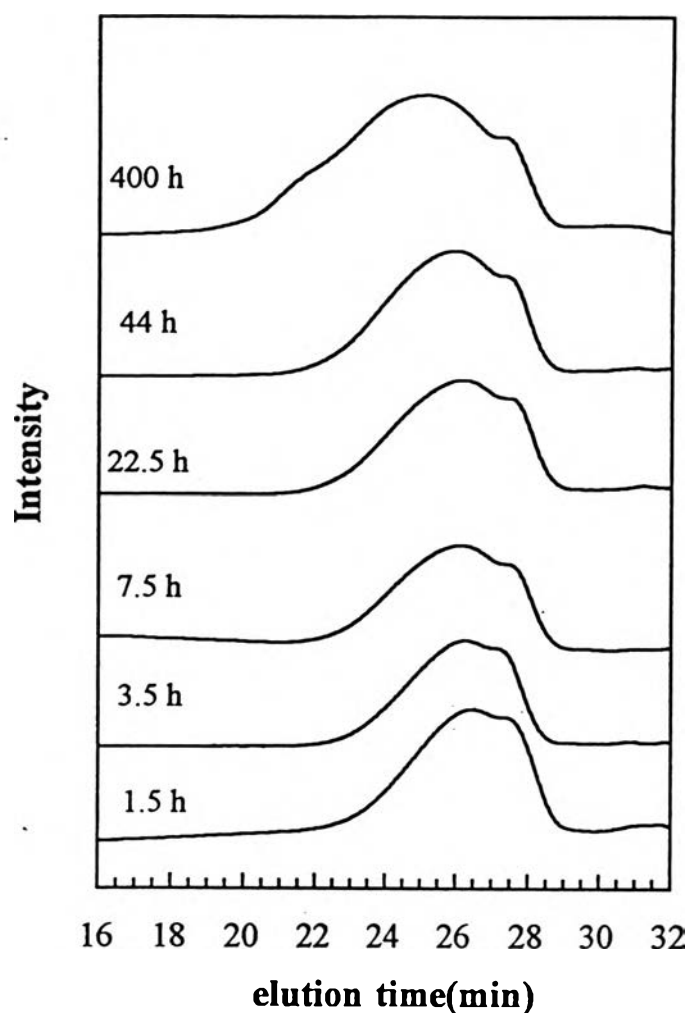


Figure 3-8 GPC chromatograms of γ -MPS oligomers at different drying time.

Comparing the system of 10 % mol PEG (Figure 3-9) to γ -MPS individual system, the shape of these two chromatograms look similar but the elution time of 10 % mol PEG is slower than the γ -MPS individual system, especially at the initial stage of drying (1.5 hours).

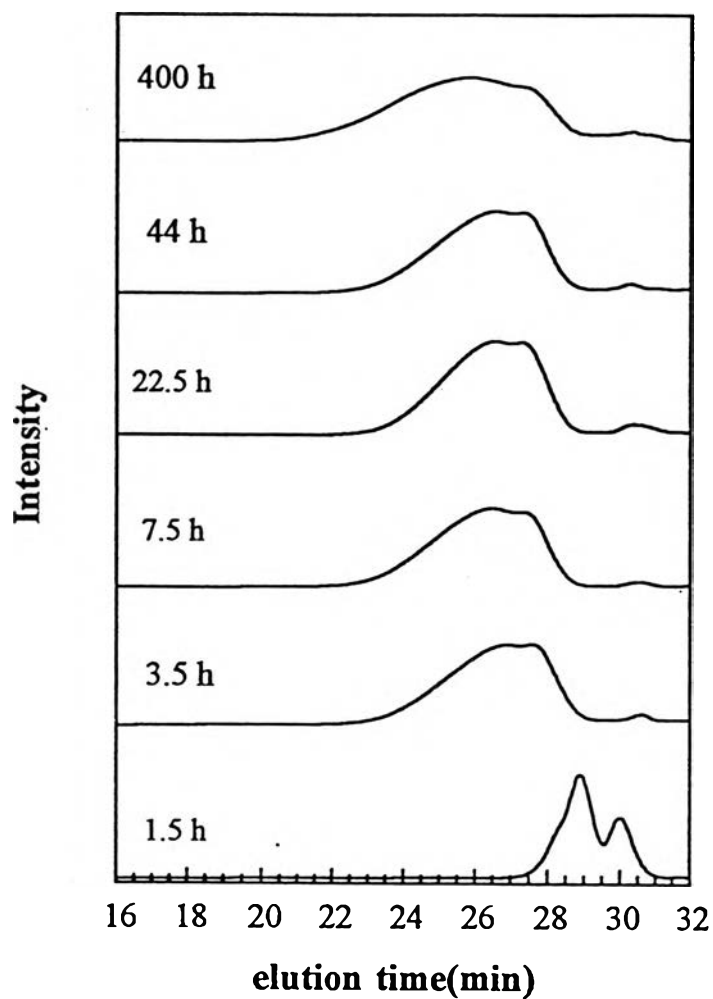


Figure 3-9 GPC chromatograms of the model system consisting of 10 % mol PEG at different drying time.

FTIR spectra of PEG, γ -MPS hydrolyzates and the mixture system between γ -MPS and PEG are shown in Figure 3-10.

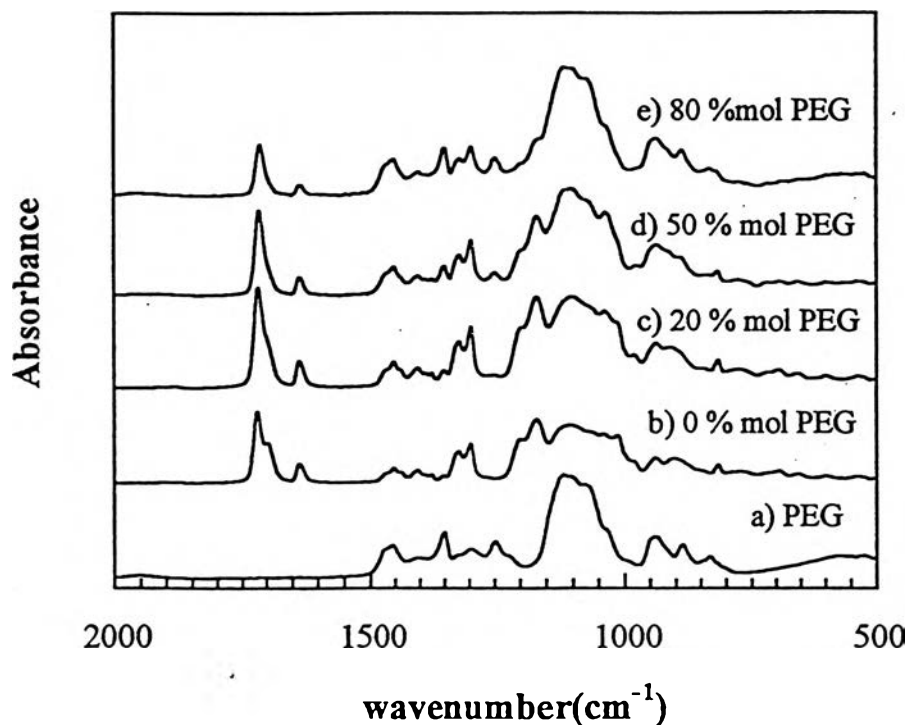


Figure 3-10 FTIR spectra of PEG, γ -MPS hydrolyzates and the model systems consisting of PEG.

In the PEG spectrum, the small bands at 1465 and 1350 cm^{-1} are considered to be $-\text{CH}_2$ asymmetric deformation and $-\text{CH}_3$ symmetric deformation respectively. The strong bands in the range of $1030\text{--}1120\text{ cm}^{-1}$ are assigned to C-O-C asymmetric stretching of PEG chain.

For γ -MPS hydrolyzates individual system, the strong bands at 1720 and 1698 cm^{-1} are due to the C=O stretching of free-carbonyl and H-bonded

carbonyl functionality respectively. The band at 1635 cm^{-1} comes from C=C stretching of γ -MPS molecules. The bands in the region $1100 - 1300\text{ cm}^{-1}$ are associated with ester functionality. The siloxane bands appear in the region $1000 - 1130\text{ cm}^{-1}$. The 941 cm^{-1} can be assigned to vinyl wagging band and the 904 cm^{-1} band is the Si-OH band.

When %mol of PEG is increased, the decrease in H-bonded carbonyl ratio is observed (Figure 3-11). Curve fitting method is applied to resolve the two overlapped carbonyl bands.

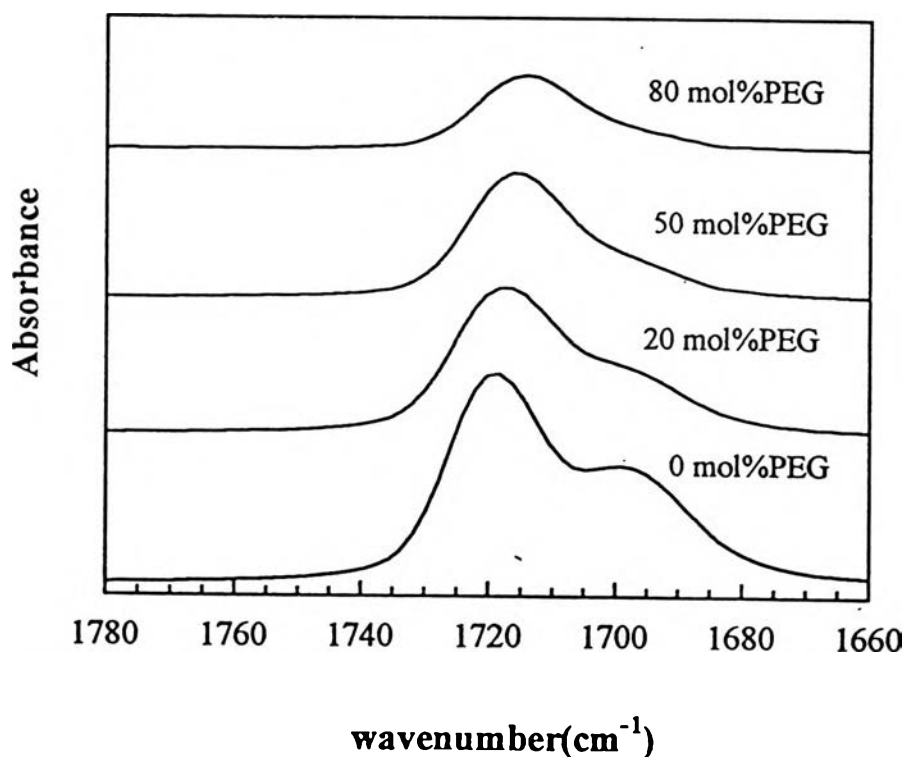


Figure 3-11. FTIR spectra of carbonyl region of the model sizing system.

Silanol groups in the γ -MPS hydrolyzate molecules are expected to form hydrogen bonding with both its own C=O groups and C-O-C in PEG chain.

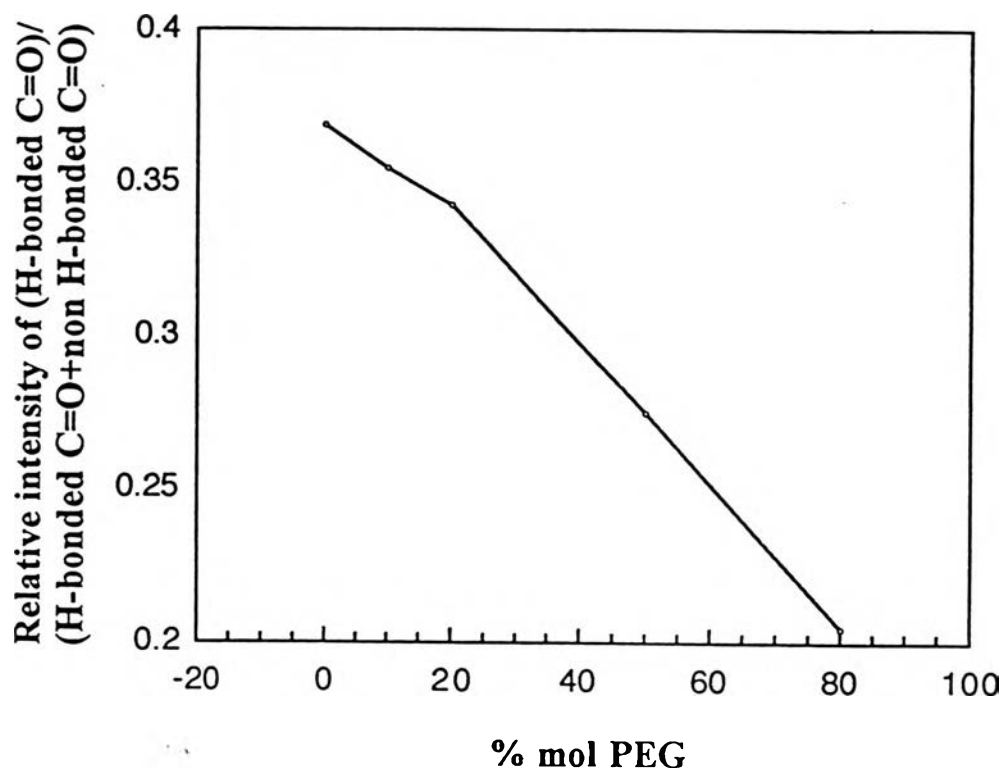


Figure 3-12 The plot of relative intensity of (H-bonded C=O) / (H-bonded C=O + non H-bonded C=O) of γ -MPS molecules ratio as a function of %mol PEG.

Figure 3-12 shows the decrease of H-bonded carbonyl with % mol PEG, the ratio of H-bonded carbonyl is gradually decreased when the % mol is increased from 0-20 % mol. After 20 % mol PEG, the ratio of H-bonded carbonyl decreases rapidly. From these results, it can be concluded that silanol groups of γ -MPS hydrolyzate prefers forming hydrogen bond with C-O-C in PEG chain to with C=O of γ -MPS. These hydrogen bonds imply the

limitation of the movement of Si-OH groups which has an effect on the condensation of Si-OH groups so that the condensation in the model system containing PEG is slower than the system without PEG. Furthermore the PEG chain in the system is considered to show the hindrance effect which interferes the mobility of γ -MPS hydrolyzate. By this effect, silanol groups are separated from each other and the condensation becomes slower.

When the contents of PEG in the system is increased up to 20 % mol (Figure 3-13), the condensation of γ -MPS hydrozates to form small oligomers such as dimers, tetramers is faster than the 10 % mol system .

There are one main peak appearing at elution time around 27.3 minutes and one small shoulder at 26 minutes. This shoulder gradually increases with drying time until its intensity is equal to the intensity of main peak. It is expected that neighboring γ -MPS hydrozates which hydrogen bond with the two adjacent oxygen atoms in PEG chain can condense with each other to form siloxane bond (hereafter called neighboring effect).

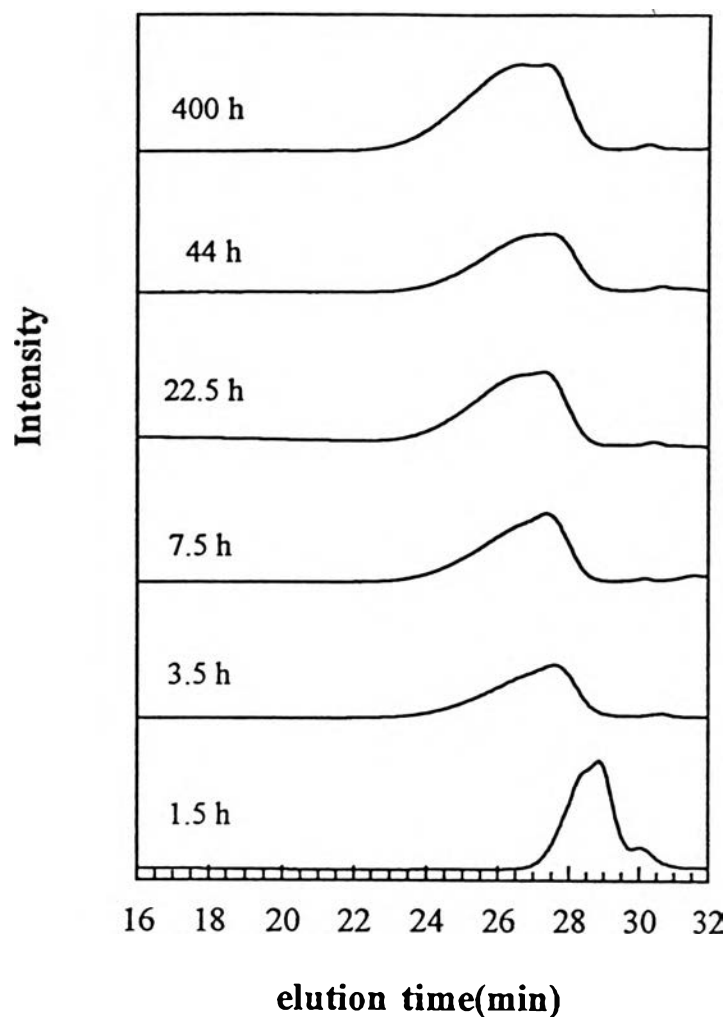


Figure 3-13 GPC chromatograms of the model system consisting of 20 mol% PEG at different drying time.

The development of γ -MPS hydrolyzate to form small oligomer in this system is higher than the 10 % mol system and γ -MPS individual system. When the drying time is increased, the solvent is evaporated, hindrance effect is found to be dominant. PEG chain in the system will interfere with the

mobility of Si-OH group thus silanol condensation is more severe in the system at less drying time.

The structure of γ -MPS hydrolyzates in the solution with PEG chain can be delineated as follows.

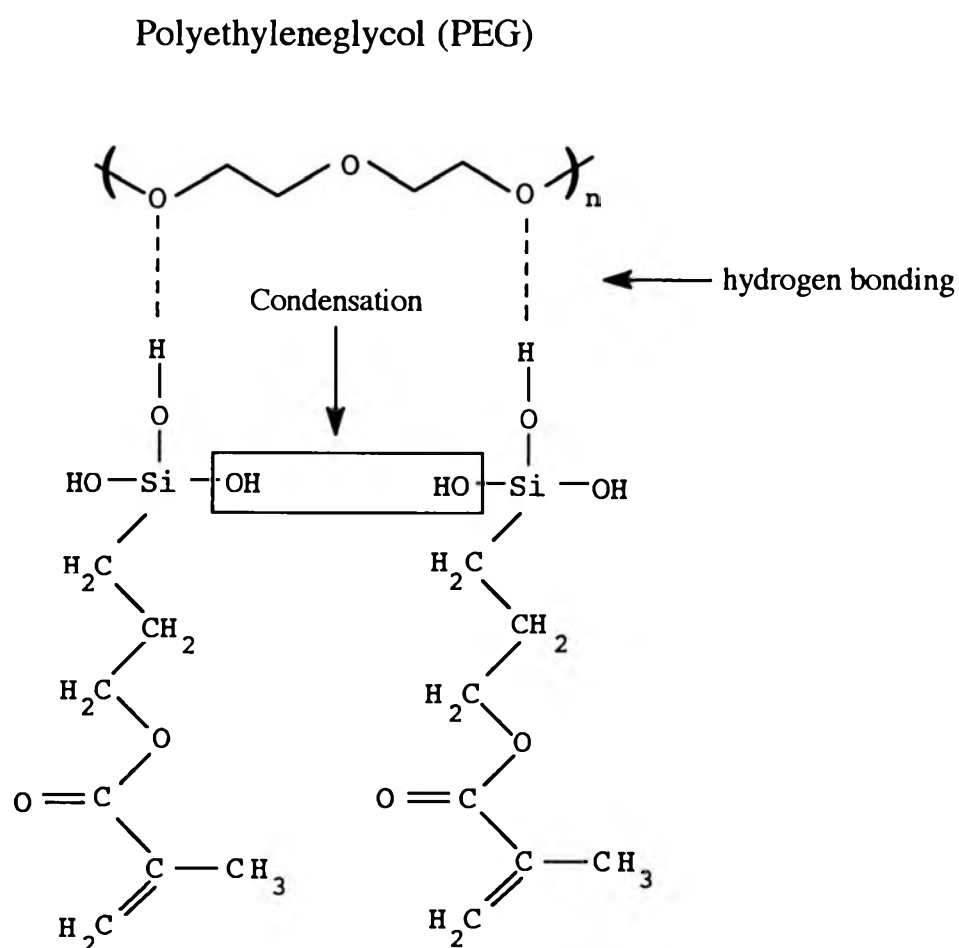


Figure 3-14. The condensation between neighboring silane molecules.

Figure 3-14 shows the effect of neighboring silane molecules enhanced by the condensation between the two adjacent γ -MPS hydrolyzate molecules which form hydrogen bonding to the adjacent oxygen atoms in PEG chain.

Figure 3-15 shows GPC chromatograms of model system with 50 % mol PEG.

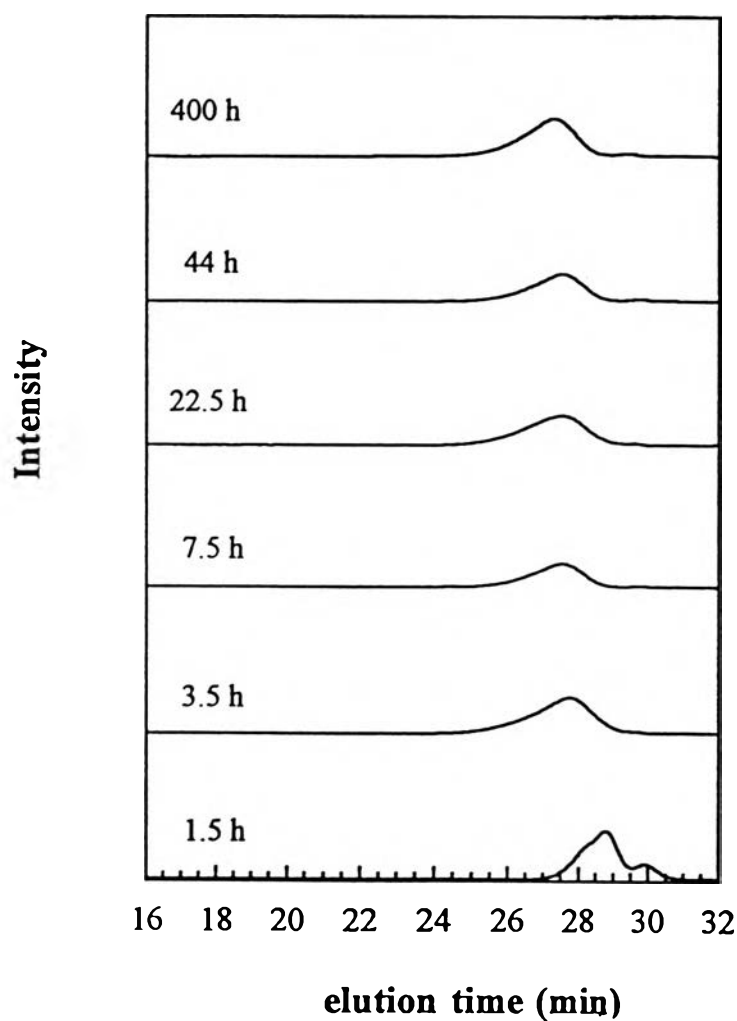


Figure 3-15 GPC chromatograms of the model system consisting of 50 % mol PEG at different drying time.

At the initial stage of drying step, γ -MPS hydrolyzate monomer is condensed with each other and the rate of oligomer formation is higher than

that of 10 % mol PEG system but less than that of 20 % mol PEG system. This suggests that neighboring effect is still the dominant effect which controls the condensation of the system but hindrance effect starts to be notable too. At drying time of 3.5 hours, the main peak at 27.5 minutes does not change much with drying time. The occurrence of higher molecular weight does not appear since the evaporation of solvent at higher drying time causes the system to have higher concentration of PEG chain. These PEG chains act as an obstacle to the condensation. They can separate the Si-OH groups from each other until condensation can not occur.

At 80 % mol , GPC chromatogram (Figure 3-16) shows the slowest condensation of Si-OH groups in the system since the composition of PEG is the highest.

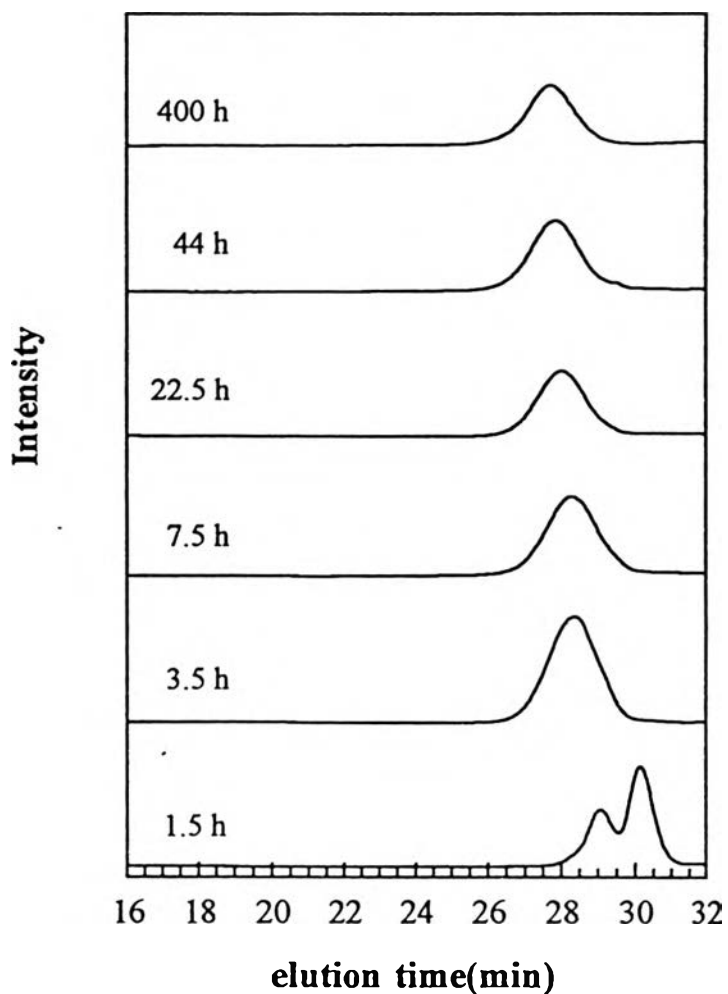


Figure 3-16 GPC chromatograms of the model system consisting of 80 mol% PEG at different drying time.

The silanol condensation is concluded to be controlled by the hindrance effect, hence the developing of molecular weight with time is very difficult.

It can be implied that there are two effects which influence the silanol condensation of the model sizing system between γ -MPS and PEG. One is the neighboring effect occurring from the condensation between neighboring molecules of silane which form hydrogen bond with the two adjacent oxygen atoms in PEG chain. This effect is considered to act as the positive effect enhancing the condensation of silanol group in the model sizing system. The other effect is the hindrance effect which is the interference of PEG chain to the encountering between silanol groups. However, PEG chains may separate silanol groups from each other so that the distance between two silanol groups is too far to condense with each other.