

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Precursor synthesis and characterization

Silatrane precursor was successfully synthesized via the Oxide One Pot Synthesis (OOPS) process by reacting SiO_2 with TEA using ethylene glycol as solvent. The reaction is given in Eq. 4.1. The FAB⁺-MS results of crude product of silatrane are presented in Table 4.1.

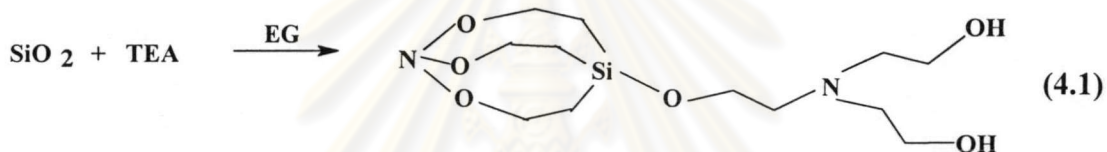


Table 4.1 The proposed structure and the pattern of fragmentation of silatrane

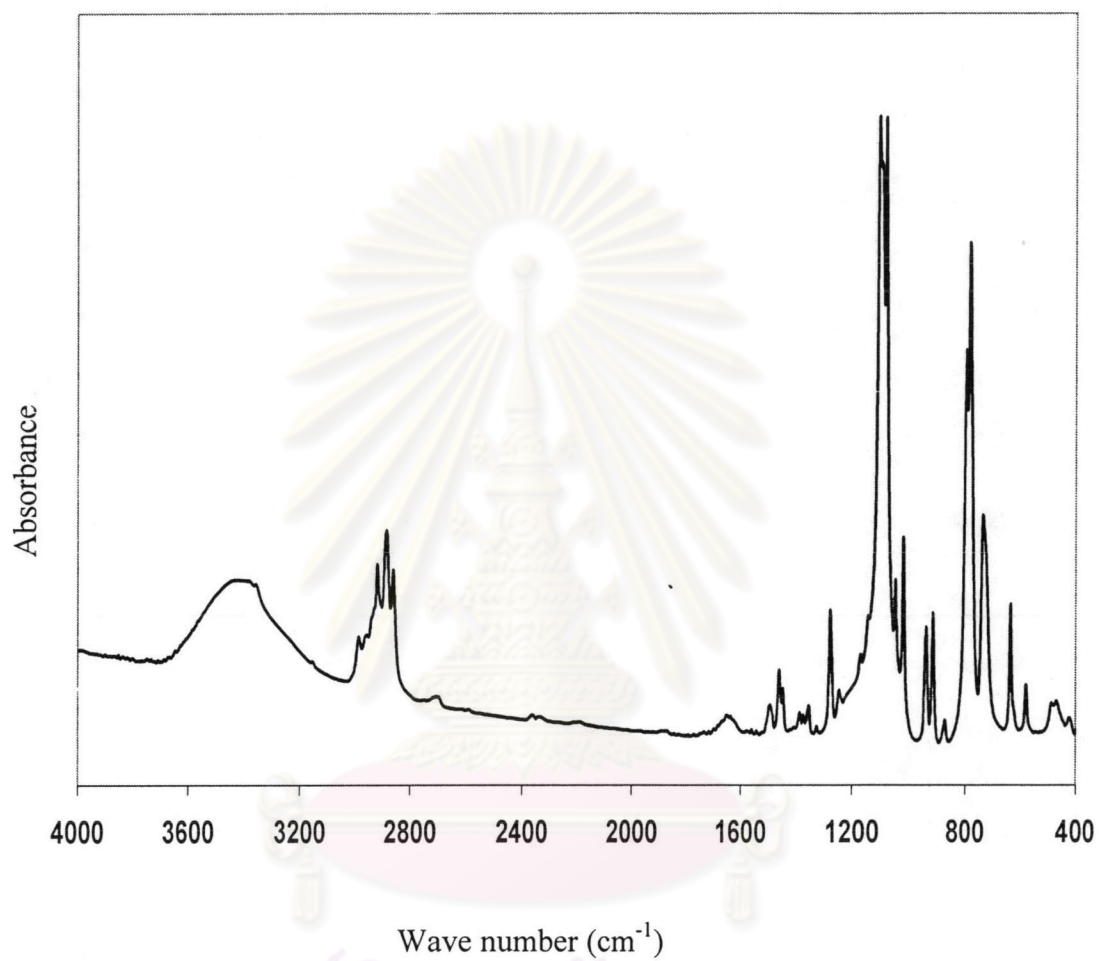
m/e	intensity	proposed structure
174	100	
236	11.3	
323	2.6	
409	0.04	

The IR spectrum of silatrane is shown in Figure 4.1. Table 4.2 provides the assignment of important functional group. FT-IR spectrum in Figure 4.1 shows the characteristic peaks of the silatrane product. The peak at 2800-2976 cm^{-1} corresponds to the C-H stretching, whereas 1380-1460 cm^{-1} results from C-H bending. The peak at 1270 cm^{-1} is assigned to C-N stretching. The strong peak at 1030-1070 cm^{-1} corresponds to the C-O stretching and the peak at 560-590 cm^{-1} refers to the Si-N bond.

Table 4.2 Infrared spectrum data of silatrane.

Characterization	Silatrane
Si-N stretching	560-590 cm^{-1}
Si-O-CH	970,883 cm^{-1}
C-O	1013-1070 cm^{-1}
Si-O-CH ₂	1015-1085 cm^{-1}
C-N	1270 cm^{-1}
C-H bending	1380-1460 cm^{-1}
C-H stretching	2800-2976 cm^{-1}

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Figure 4.1 FT-IR spectrum of silatrane

TGA themogram of silatrane is shown in Figure 4.2. Silatrane gives only one transition of weight loss at around 400°C, corresponding to the decomposition of organic ligand, $\text{Si}((\text{OCH}_2\text{CH}_2)_3\text{N})_2\text{H}_2$. The ceramic yield was around 18-22%.

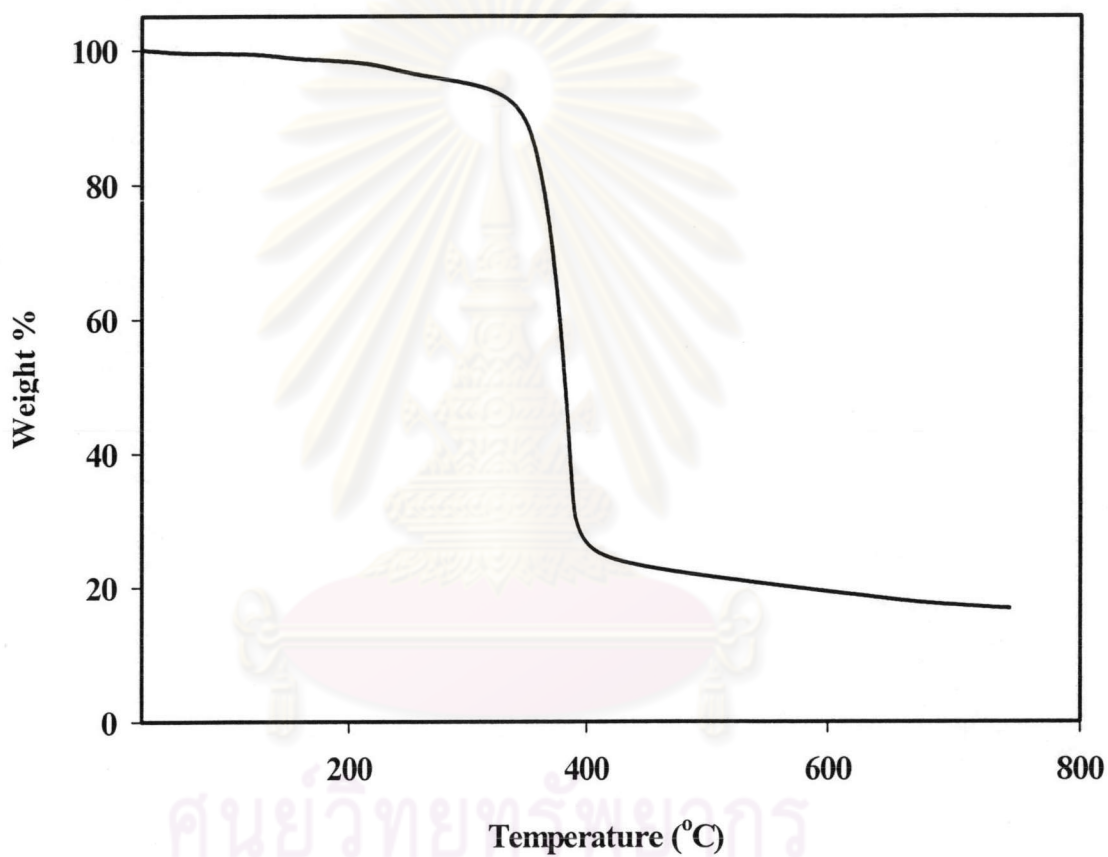
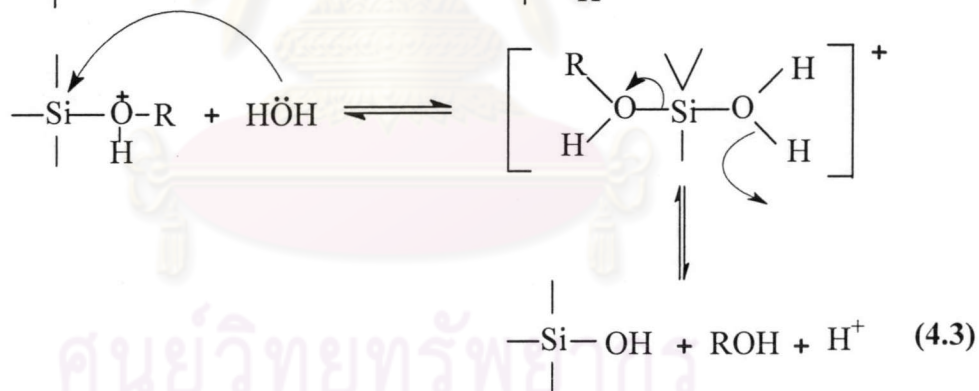
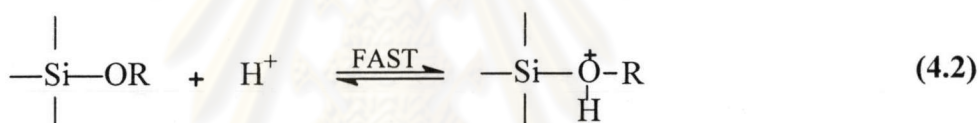


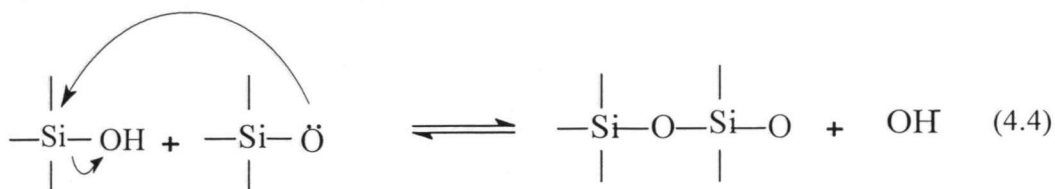
Figure 4.2 TGA profile of silatrane.

4.2 Coating solution preparation

The mixture of coating solution was hydrolyzed (and partially hydrolyzed) monomer then undergoes condensation reactions to form dimer and larger oligomers. The hydrolyzed solution was stable for hours or several days at pH about 4 followed by aging and pH adjustment to 8-9. Under acidic conditions, it is likely that an alkoxide group is protonated in a rapid first step. Electron density is withdrawn from the silicon atom, making it more electrophilic and thus more susceptible to be attacked by water. This results in the formation of a penta-coordinate transition state with significant SN₂-type character. The transition state decays by displacement of an alcohol and inversion of the silicon tetrahedron, as shown in Eqs. 4.2 and 4.3.



Then polymerization to form siloxane bonds occurs by either an alcohol-producing or a water-producing condensation reaction. The condensation reaction involves the attack of a nucleophilic deprotonated silanol on a neutral silicic acid as shown in Eq. 4.4.



The prepared solution was deposited onto PMMA substrates by dipping-withdrawing manner at the room temperature. The coating film achieved on PMMA was transparent and smooth.

4.3 Characterization of coating solution

FTIR technique was used to investigate the sol-gel reactions and follow the transformation of main chemical during this process. The result is shown in the Figures 4.3 and 4.4.

The time dependence of infrared spectra for the silatrane coating solution is shown in Figure 4.3. The hybrid precursor exhibits the peaks of a hydroxyl group at 3400 cm^{-1} , indicating that hydrolysis of a methoxy moiety occurred. The Si-O-CH₃ group is recognized by a small band at about $1170\text{--}1160 \text{ cm}^{-1}$ together with small bands in the range $1100, 1075(\text{s}),$ and $970\text{--}940 \text{ cm}^{-1}$. One or more very strong infrared bands in the region $1200\text{--}1100 \text{ cm}^{-1}$ were observed due to the presence of siloxane. The Si-O-Si absorption at $1200\text{--}1100 \text{ cm}^{-1}$ become broader and more complex (two or more overlapping band) with time due to the longer and branched siloxane chain [25-27].

The spectra in Figure 4.3 also indicated that firstly, hydrolysis reaction occurred and condensation reaction was observed at about 3 h. The peak intensities of Si-O(H) stretching at 900 cm^{-1} and the (Si)O-H stretching at 3400 cm^{-1} corresponding to the hydrolysis of methoxy group in GPTS/silatrane solution were increased with increasing reaction time. (the partial condensation). The Si-O-Si asymmetric stretching at $1200\text{--}1100 \text{ cm}^{-1}$ and the Si-O-Si symmetric stretching at 870 cm^{-1} confirm the occurrence of partial condensation. Finally, partially condensed

GPTS/silatrane solution with free silanol groups and H-bonded silanol groups was obtained at 24 h reaction time.

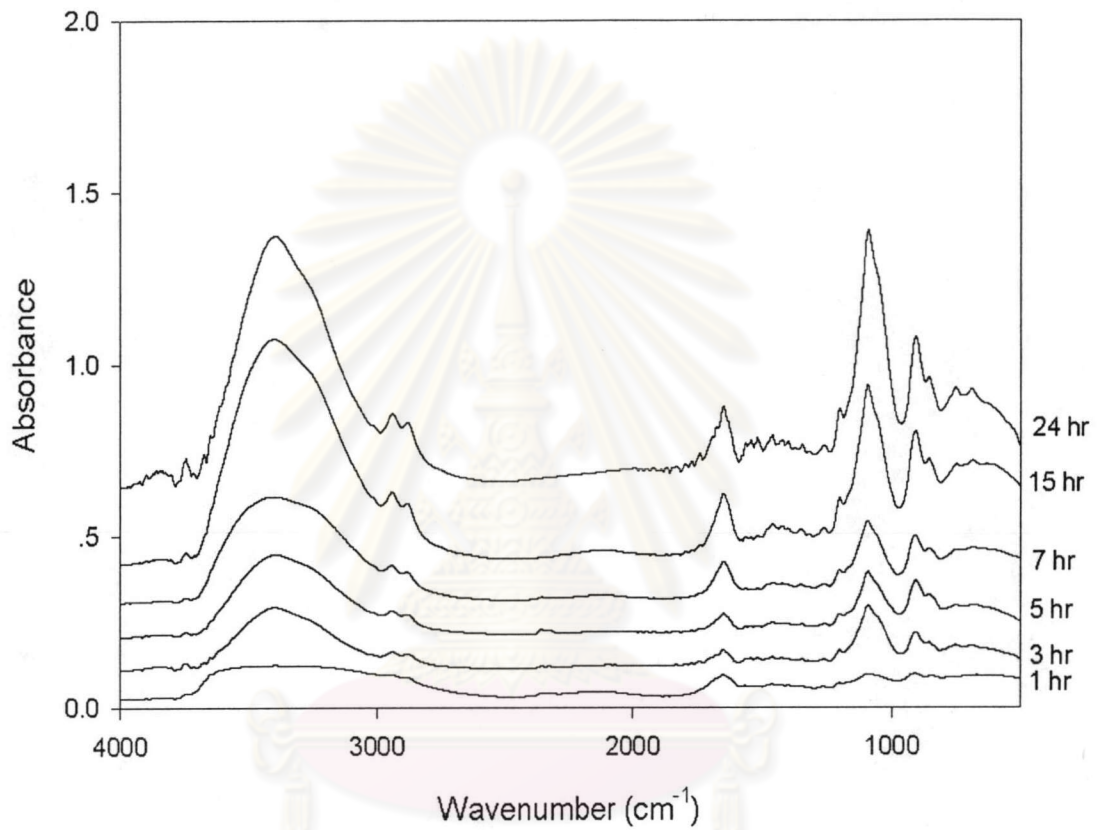


Figure 4.3 FT-IR spectra of silatrane coating solutions at GPTS / silatrane ratio of 1. Data are shown at various time after adding GPTS to the solution of silatrane.

Figure 4.4 shows the dependence of infrared spectra on GPTS/silatrane ratio for the silatrane coating solution. These data were taken at reaction time of 24 h and APS was added. The silatrane coating solution with the GPTS/silatrane ratio higher than 3 exhibited high intensity at 3400 cm^{-1} of Si-OH band. As GPTS/silatrane ratio increased, the intensity increased, indicating that the surface silanol increased. The data also show that the intensity of Si-O-Si band in the region of $1200\text{-}1100\text{ cm}^{-1}$ increased with increasing GPTS/silatrane ratio.

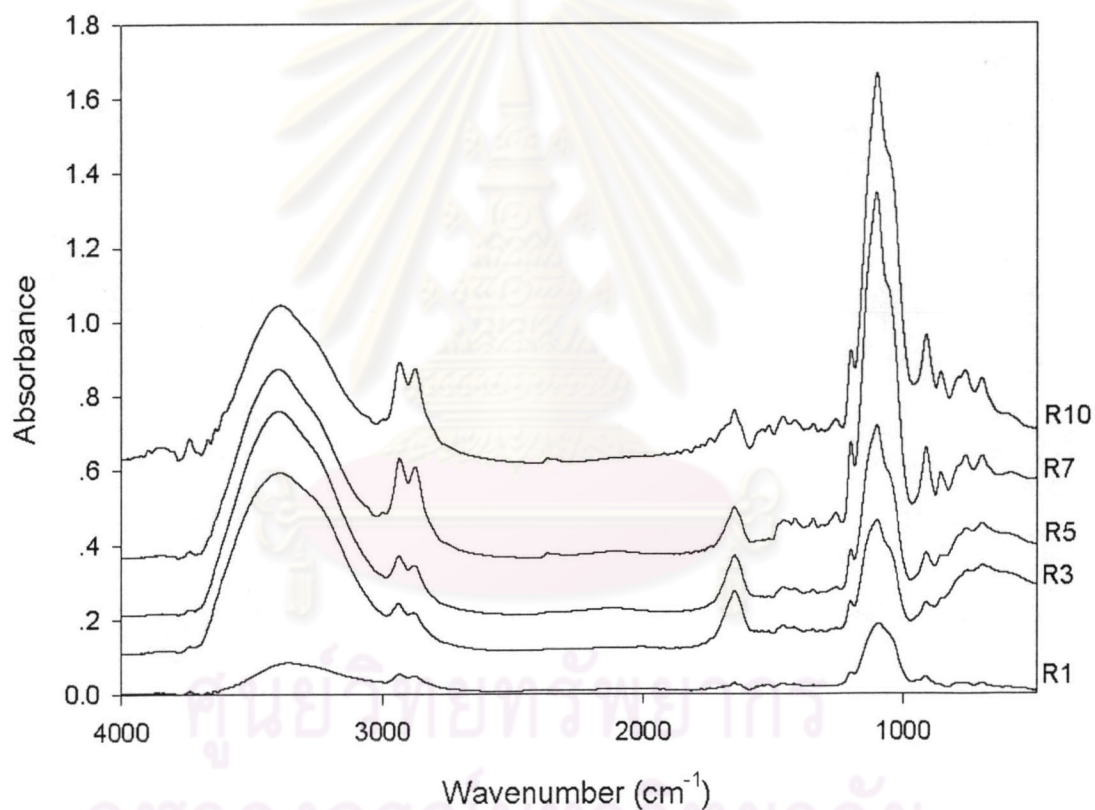


Figure 4.4 FT-IR spectra of the silatrane coating solution at various GPTS/silatrane ratio. Data were taken at 24 h after addition of GPTS.

Silatrane coating solution modified with GPTS has epoxy functionality which can be cross-linked by an amine curing agent (APS). As discussed above, silatrane solution prepared with GPS addition at pH 4 followed by aging and pH adjustment to 8-9 was stable for several days. However, when the amine curing agent was added, the suspension became gel (i.e., semisolids which did not flow). The effect of GPTS/silatrane ratio ($R=0-10$) on gel time of coating solution containing a constant relative amount of APS (3 wt% of total weight) was also investigated. The results showed that the gelation time decreased from about 200 h for the suspension with GPTS/silatrane ratio of 1 ($R=1$) to 40 h for the suspension with GPTS/silatrane ratio of 10 ($R=10$).

For the coating solution without APS addition, no gel formed for all GPTS/silatrane ratio, indicating that the solution enhanced silanol condensation accompanying pH adjustment to 9 was not responsible for the gelation. Therefore, the gelation of GPTS-modified silatrane solution is related to the curing of the epoxy-functionalized particles and silane species in solution. For the preparation of coating solution, the reactivity of the amine and epoxy groups at room temperature indicates that the time available to form the coating will be limited by the amount of GPTS and amine present. [28-29]

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4.4 The evaluation of coated PMMA

When the GPTS solution without silatrane was used, the appearance of thin film formed on PMMA substrate was transparent. This film was easily pulled off from the substrate. It can be explained that GPTS and APS formed siloxane bond (Si-O-Si) was dimer or oligomers, when silatrane was added, the siloxane bond in the pattern of networks was formed.

4.4.1 Adhesion test

The cross-cut tape test was used to evaluate the percentage area removed after pulling the tape off. Classification of adhesion test results is shown in Table A. (Appendix A)

The temperature and curing time have an effect on adhesion of coated PMMA. The results are present in Table 4.2. From the results, the samples coated with the solution at GPTS/silatrane ratio of 1 ($R=1$) and 80°C exhibit poor adhesion at curing time in the range of 1 to 3 hours. However, as the temperature increased to 120°C , the better adhesion was achieved at curing time of 2 h. Therefore, the appropriate curing condition in this experiment for adhesion test was at 120°C for 2 h. The same results were observed for other GPTS/silatrane ratio ($R = 3, 5, 7$ and 10) as shown in Table 4.3.

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Table 4.3 The effect of curing time and temperature on the coated PMMA.

Composition	Curing temp. (°C)	Curing time (hours)		
		1	2	3
GPTS/silatrane = 0 (R0)	80	0B	0B	0B
	100	0B	0B	0B
	120	0B	0B	0B
GPTS/silatrane = 1 (R1)	80	0B	0B	0B
	100	0B	0B	5B
	120	0B	5B	5B
GPTS/silatrane = 3 (R3)	80	0B	0B	0B
	100	0B	0B	5B
	120	0B	5B	5B
GPTS/silatrane = 5 (R5)	80	0B	0B	0B
	100	0B	0B	5B
	120	0B	5B	5B
GPTS/silatrane = 7 (R7)	80	0B	0B	0B
	100	0B	0B	5B
	120	0B	5B	5B
GPTS/silatrane = 10 (R10)	80	0B	0B	0B
	100	0B	0B	5B
	120	0B	5B	5B

Table 4.4 shows the effect of GPTS/silatrane ratio on the state of coating film. It can be seen that for the GPTS/silatrane ratio higher than 1, the measured percentage area removed was 0%, which is categorized in the 5B level. For the coating solution without silatrane, the measured percentage area removed was 100%, which is categorized in the 0B level. Thus, addition of GPTS to the silatrane solution at various ratios yield transparent film and good adhesion to the substrates except the film obtained from coating solution without silatrane (R0).

Table 4.4 The state of coating films on PMMA substrate for various ratios of GPTS/silatrane.

Composition	GPTS/silatrane	Adhesion test	Formation of coating films
R0	0	0B	Transparent
R1	1	5B	Transparent
R3	3	5B	Transparent
R5	5	5B	Transparent
R7	7	5B	Transparent
R10	10	5B	Transparent

Curing temperature = 120°C, Curing time = 2 h

It can be explained that this precursor could improve the adhesion between the interface of coating solution and PMMA substrate. The APS may also be extended to PMMA substrate. On this occasion, however, APS reacts with the ester groups and became linked to the substrate through amide groups. While GPTS coupling agent was able to form strong bond to the inorganic precursors and also to surrounding polymer substrates, linking the different materials together. Figure 4.5 shows the GPTS forming strong bond to inorganic precursor.

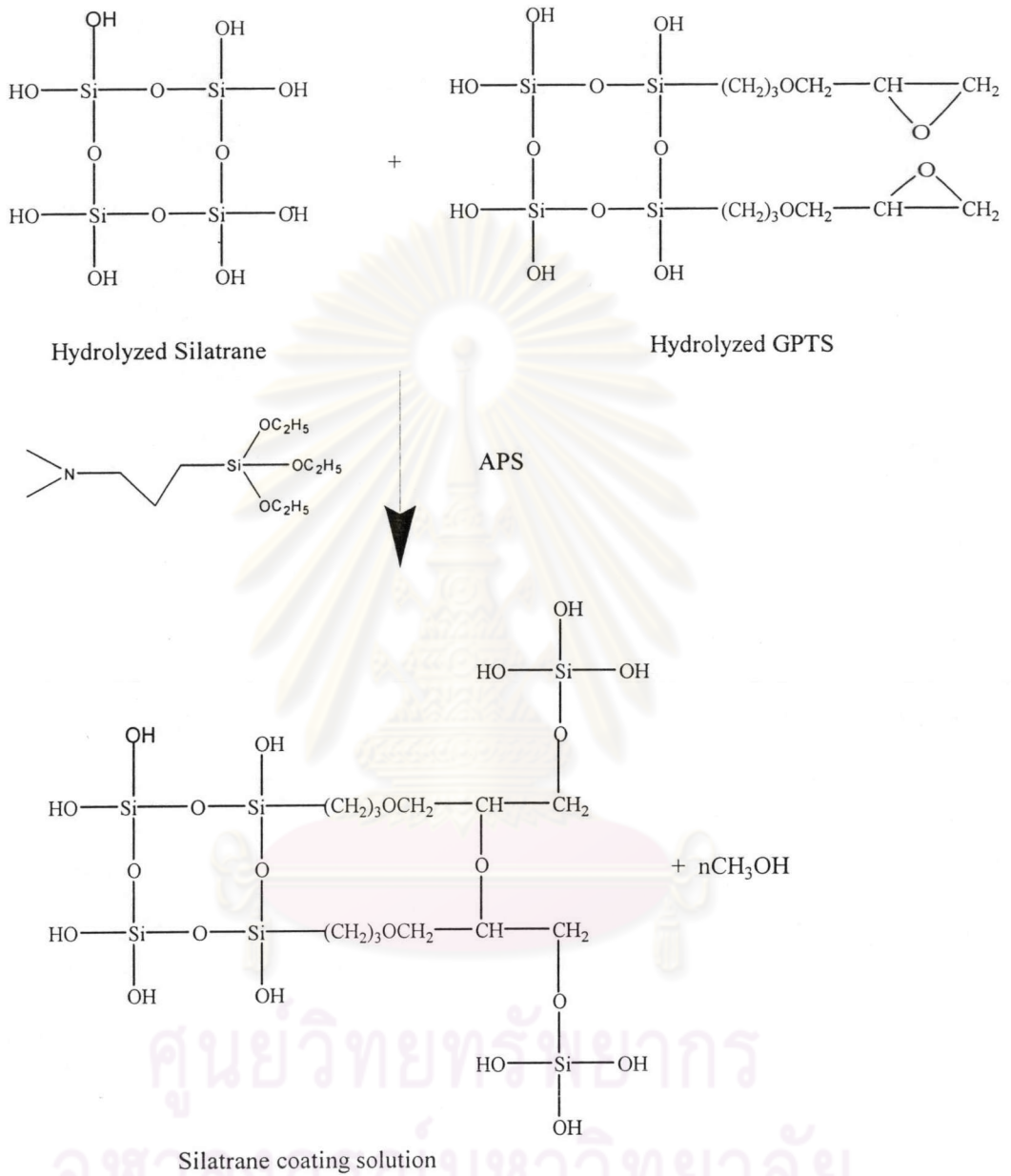


Figure 4.5 GPTS forming strong bond to silatrane precursor

4.4.2 Steel wool scratch test

The steel wool scratch test was used to evaluate the scratch resistance of PMMA coated. The standard of steel wool scratch test is shown in Table B. (Appendix B)

The effect of curing temperature and curing time on the scratch resistance is present in Table 4.5. For the samples coated with solution at GPTS/silatrane ratio of 0, 1, 3, 5, 7 and 10, the scratch resistance increased with curing temperature (80-120°C) for the curing time in the range of 1 to 3 h. However, at temperature 120°C, the scratch resistance increased with increasing curing time for the solution at GPTS/silatrane ratio in the range of 1 to 10. Therefore, the appropriate curing condition in this experiment for best scratch resistance was at 120°C for 2 h.

Table 4.6 shows the effect of GPTS/silatrane ratio on scratch resistance and uncoated PMMA substrate; the level of hardness after the test was carried out according to 10 cycles of testing.

From Table 4.6, the uncoated PMMA substrate exhibited poor scratch resistance, scratch line was observed when the load was applied (Figure 4.6a). Figure 4.6 also shows the transmission optical micrograph of coated PMMA with various GPTS/silatrane ratio and uncoated PMMA substrate before and after steel wool scratch test. It can be seen that the scratch resistance of coating film increased with an increase in GPTS/silatrane ratio (Figure 4.6c – 4.6g). The enhancement of scratch resistance is caused by that silane treatment lowers the surface energy of the silica suspension, which reduces capillary stresses during drying. The scratch damage should cause neither delamination of the coating nor damage of the substrate. Therefore, it could be concluded that the organic-inorganic hybrid coating film consisting of silatrane, GPTS and 3-APS formed a high dense siloxane network between particles, resulting in good scratch resistance.

Table 4.5 The effect of curing time and temperature on the coated PMMA.

Composition	Curing temp. (°C)	Curing time (hours)		
		1	2	3
GPTS/silatrane = 0 (R0)	80	F	F	E
	100	F	E	E
	120	E	D	D
GPTS/silatrane = 1 (R1)	80	F	E	E
	100	E	C	C
	120	D	B	B
GPTS/silatrane = 3 (R3)	80	E	D	D
	100	D	D	C
	120	C	A	A
GPTS/silatrane = 5 (R5)	80	E	C	C
	100	D	C	B
	120	C	A	A
GPTS/silatrane = 7 (R7)	80	D	C	C
	100	D	B	B
	120	B	A	A
GPTS/silatrane = 10 (R10)	80	E	C	B
	100	C	B	B
	120	B	A	A

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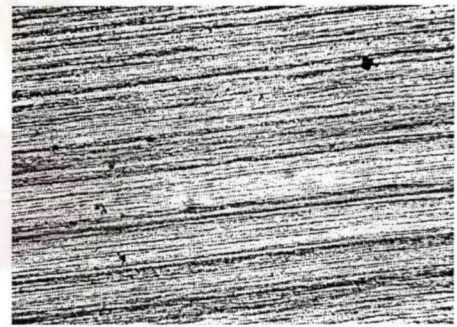
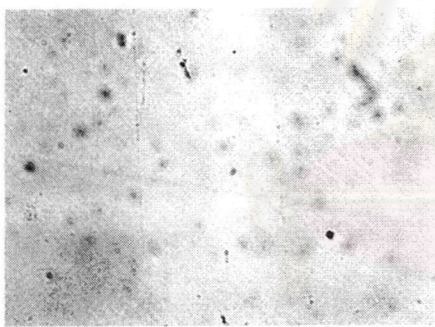
Table 4.6 The effect of GPTS/silatrane ratio on scratch resistance. (See Figure 4.6)

Composition	Steel wool test
Uncoated PMMA	F
R0	E
R1	B
R3	A
R5	A
R7	A
R10	A

Curing temperature = 120°C, Curing time = 2 h

Before

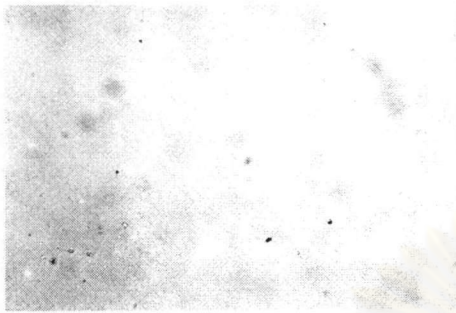
After



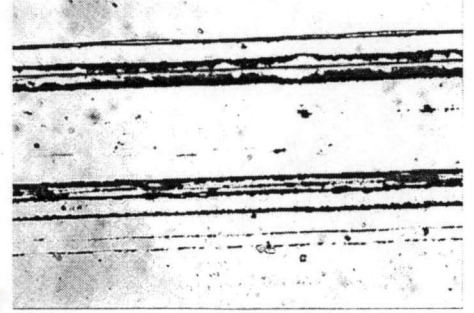
a) Uncoated PMMA

Figure 4.6 Transmission optical micrographs of PMMA substrates: before and after the steel wool scratch test.

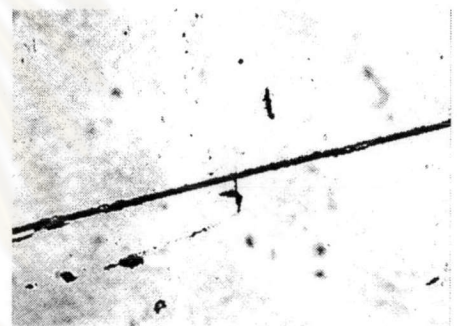
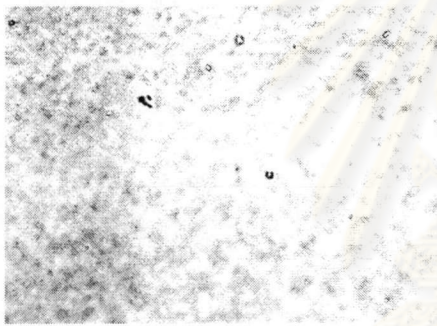
Before



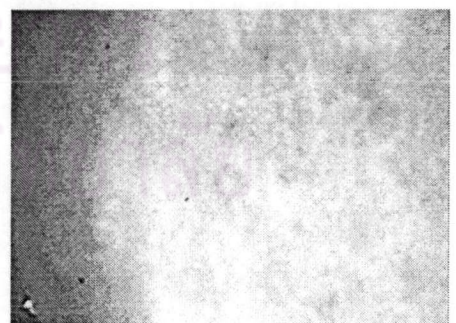
After



b) PMMA coated with GPTS/silatrane = 0 (R0)



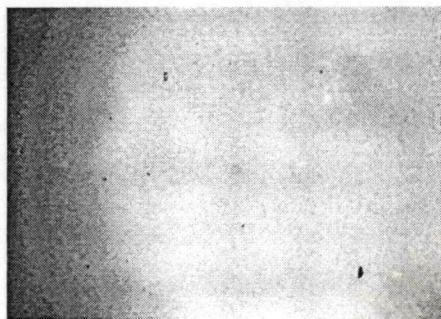
c) PMMA coated with GPTS/silatrane = 1 (R1)



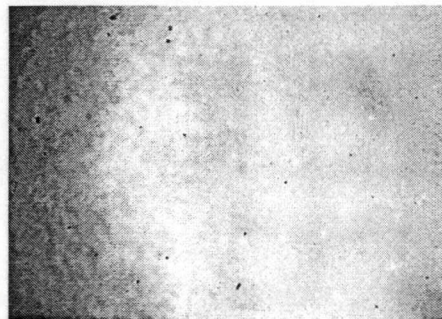
d) PMMA coated with GPTS/silatrane = 3 (R3)

Figure 4.6 (Continued)

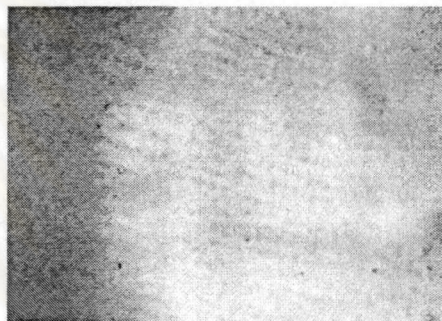
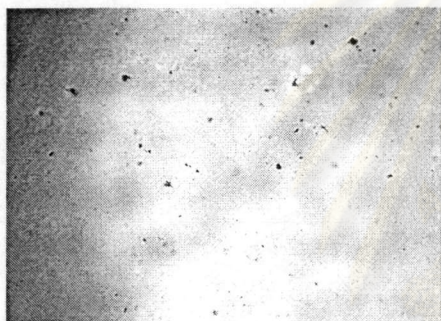
Before



After



e) PMMA coated with GPTS/silatrane = 5 (R5)



f) PMMA coated with GPTS/silatrane = 7 (R7)



g) PMMA coated with GPTS/silatrane = 3 (R3)

Figure 4.6 (Continued)