CHAPTER IV
# RESULTS AND DISCUSSION

4.1 Characterization of Synthesized Products

The synthetic procedures were followed Sun's work, and prior to study of volumetric property, synthesized products were identified using FTIR, NMR and TGA, as described following.

4.1.1 FTIR

The white powder products of spirosilicate and aminospirosilicate derivatives were characterized by mixing with KBr. As shown in Figure 4.1, all spectra showed specific characteristic peaks at 1100 and 886 cm^{-1} which are assigned to Si-O-C stretching and the peak at 3300 cm^{-1} is belonged to O-H stretching which occurs from moisture absorbed by products. From Figures 4.1b and 4.1c, the aminospirosilicate derivatives show more specific peaks around 1400 - 1700 cm^{-1} which can be referred to N-H asymmetric stretching of NH$_2$, and a broad peak at 3300 cm^{-1} corresponding to N-H symmetric stretching of NH$_2$ in the structure.
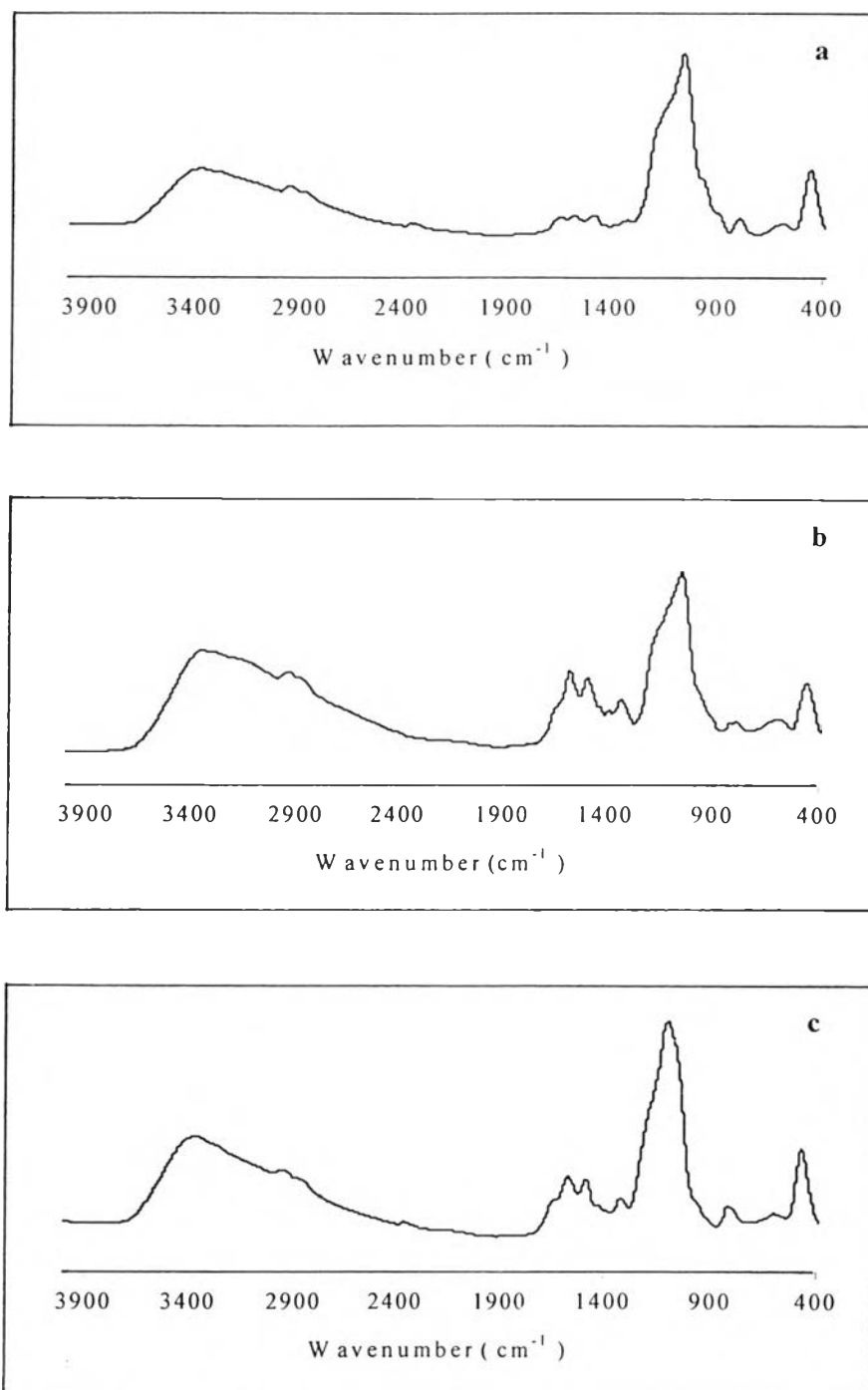
Figure 4.1 FTIR spectra of a) spirosilicate C2, b) aminospirosilicate C3 and
c) aminospirosilicate C4 products.

4.1.2 ^{1}H- and ^{13}C-NMR

The spectrum of ^{1}H and ^{13}C NMR of spirosilicate, aminospirosilicate C3 and aminospirosilicate C4 are shown in Figure 4.2, 4.3 and 4.4, respectively. The results are summarized in the Table 4.1.
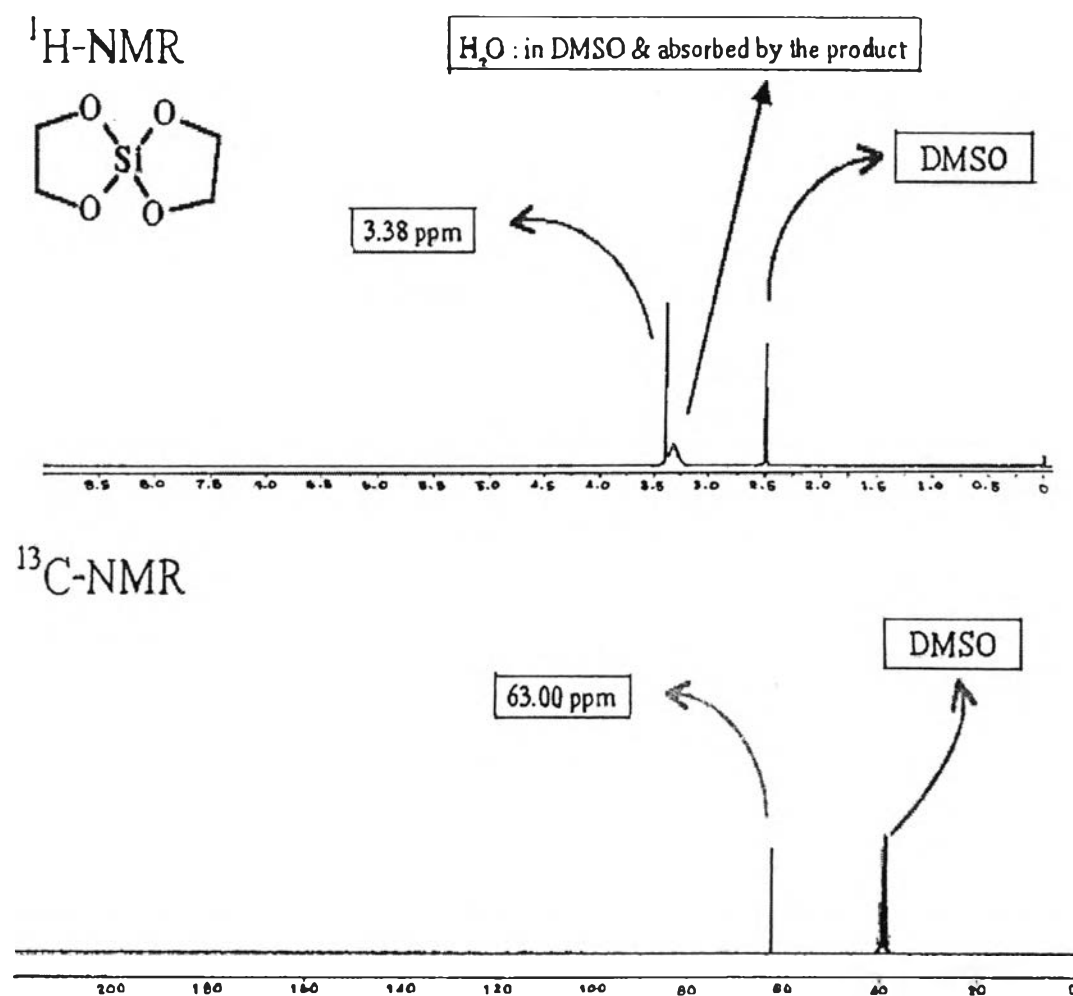

Figure 4.2 ^{1}H- and ^{13}C-NMR spectra of spirosilicate C2 product.

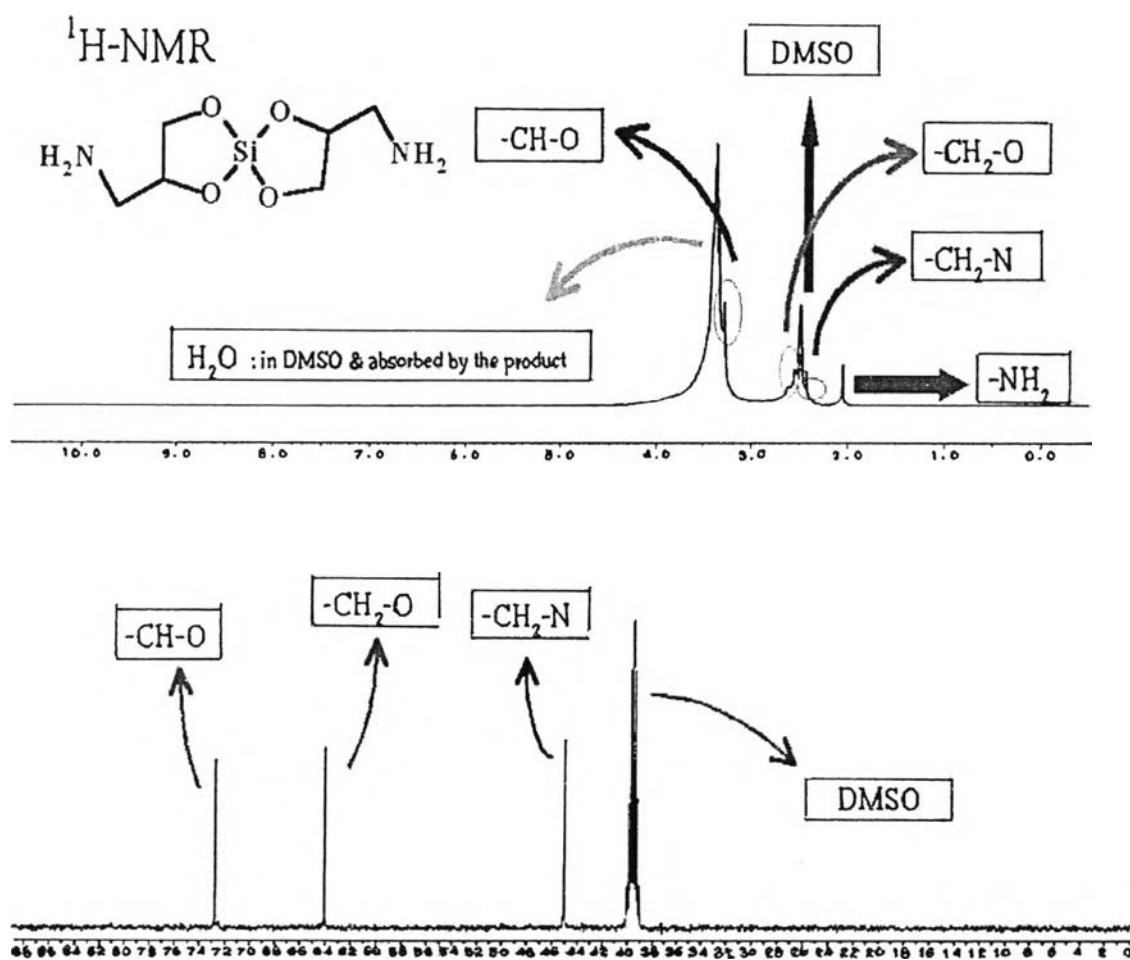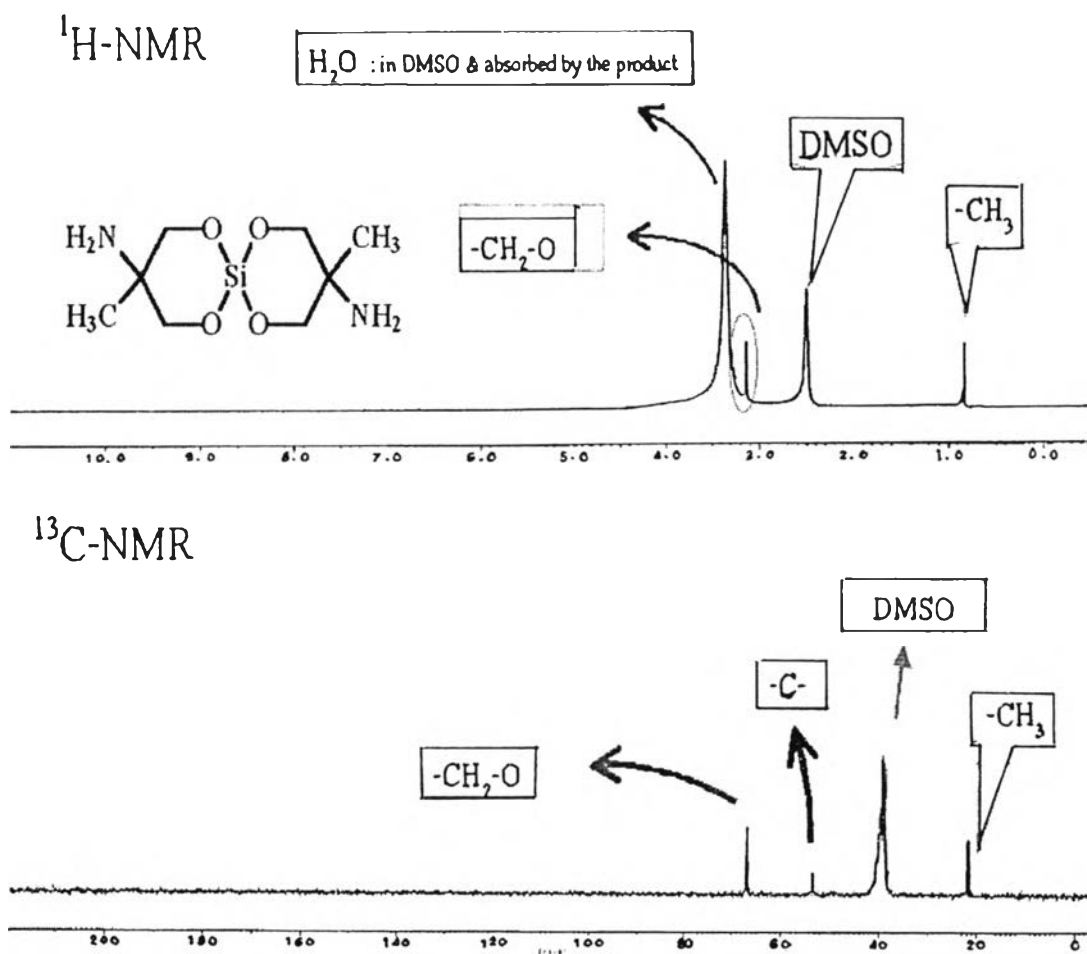**Figure 4.3** ^{1}H- and ^{13}C-NMR spectra of aminospirosilicate C3 product.

Figure 4.4 ^{1}H- and ^{13}C-NMR spectra of aminospirosilicate C4 product.

Table 4.1 The results from ^{1}H- and ^{13}C-NMR of spirosilicate and
aminospirosilicate derivatives.

| Product	Chemical Shift (ppm)		Assignment
	^{1}H-NMR	^{13}C-NMR	
C2	3.34	62.75	methylene group connecting to oxygen atom
C3	2.05	-	amine group
	2.45	44.90	methylene group connecting to nitrogen atom
	2.61	64.02	methylene group connecting to oxygen atom
	3.29	72.68	methine group connecting to oxygen atom
C4	0.83	21.99	methyl group
	3.13	67.08	methylene group connecting to oxygen atom
	-	53.47	methine group connecting to nitrogen atom

4.1.3 TGA

The thermogravimetric analysis was applied for the study of %ceramic yield of inorganic product in the crosslinking structure. This method is used to support the structural results obtained from FTIR and NMR, as can be seen in Figure 4.5. Theoretical calculation of %ceramic yield is shown in Appendix I. %Ceramic yield of spirosilicate C2, aminospirosilicate C3 and aminospirosilicate C4 are summarized in Table 4.2

**Table 4.2** %Ceramic yield from calculation as compared to experiment's data.

Product	%Ceramic yield	
	Calculation	Experiment
C2	40.05	45.02
C3	29.15	32.41
C4	25.14	26.76

As the results from FTIR, NMR and TGA, it can be concluded that spirosilicate and aminospirosilicate derivatives, whose structures are shown in Figure 4.6, are synthesized successfully.
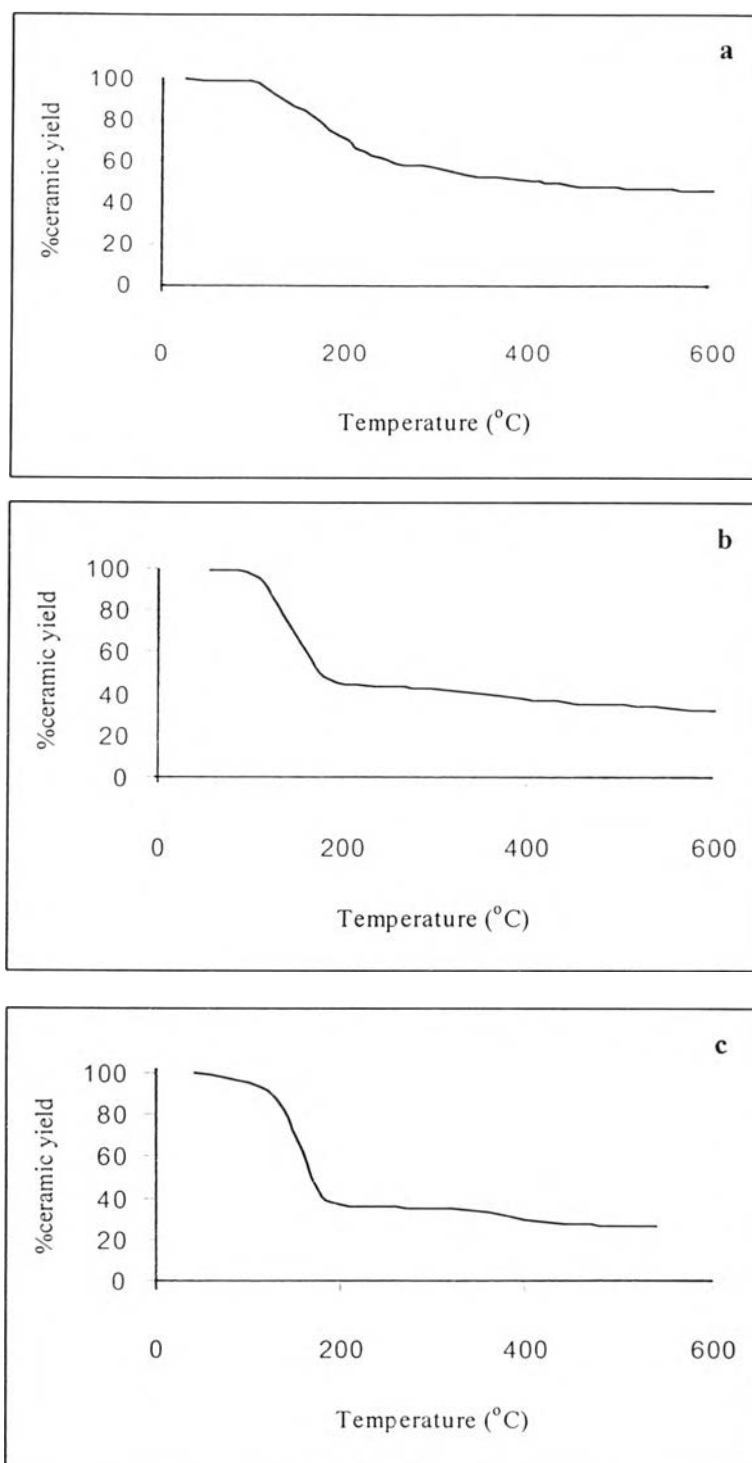
Figure 4.5 Thermograms of a) spirosilicate C2, b) aminospirosilicate C3
and c) aminospirosilicate C4.
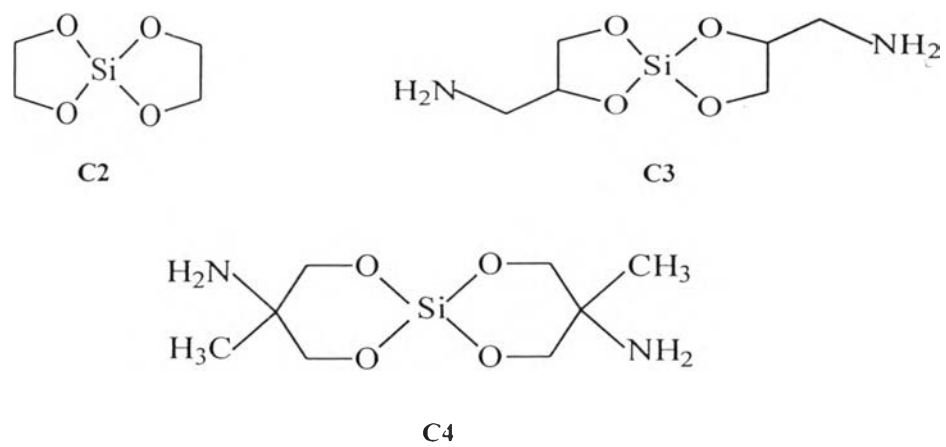
Figure 4.6 Chemical structures of spirosilicate C2, aminospirosilicate C3 and aminospirosilicate C4 products.

4.2 Study of Curing Conditions

The synthesized products of spirosilicate, aminospirosilicates from 3-amino-1,2- propanediol and from 2-amino-2-methyl-1,3-propanediol, as referred to C3 and C4, respectively, were used further in the density measurement to compare with their corresponding polymers obtained from curing. Finding the optimum conditions for curing the products was first conducted by studying the variation of curing temperature and time. For spirosilicate C2 product, the results are presented in Figures 4.7 and 4.8.
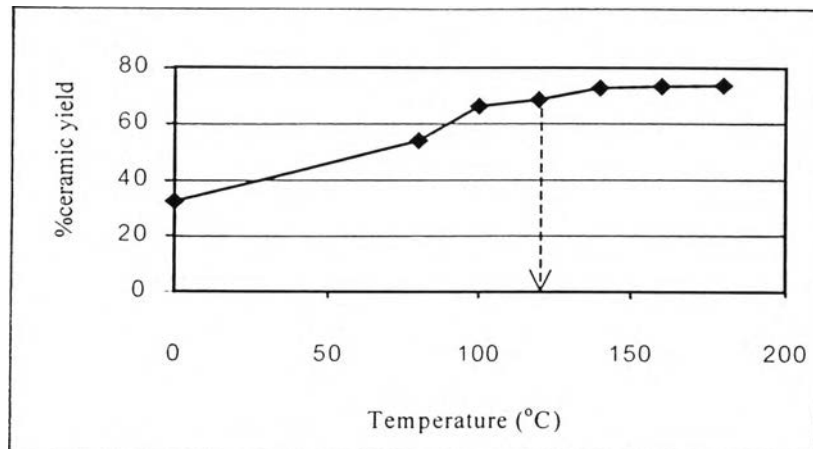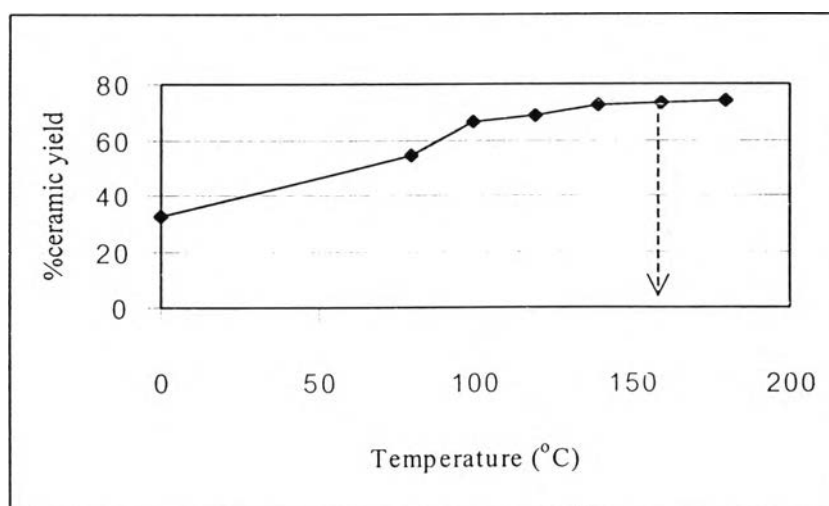
Figure 4.7 Relationship between curing temperature and %ceramic yield of spirosilicate C2 product.
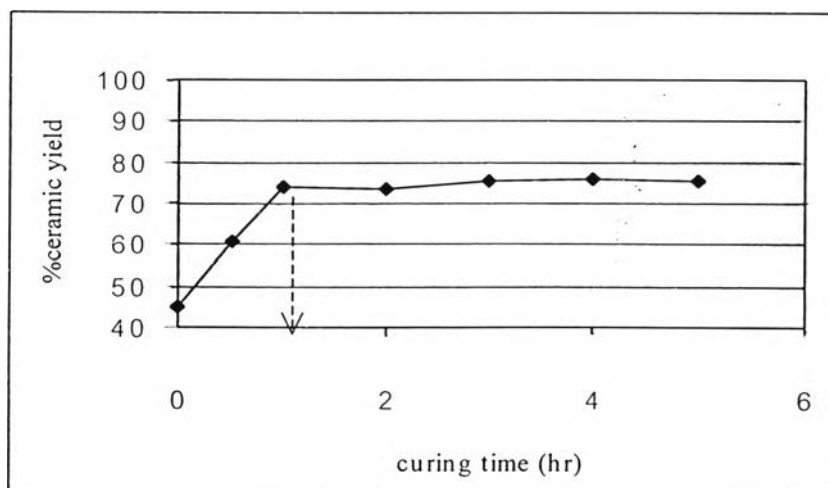
Figure 4.8 The plot of curing time vs. %ceramic yield of spirosilicate C2 product.
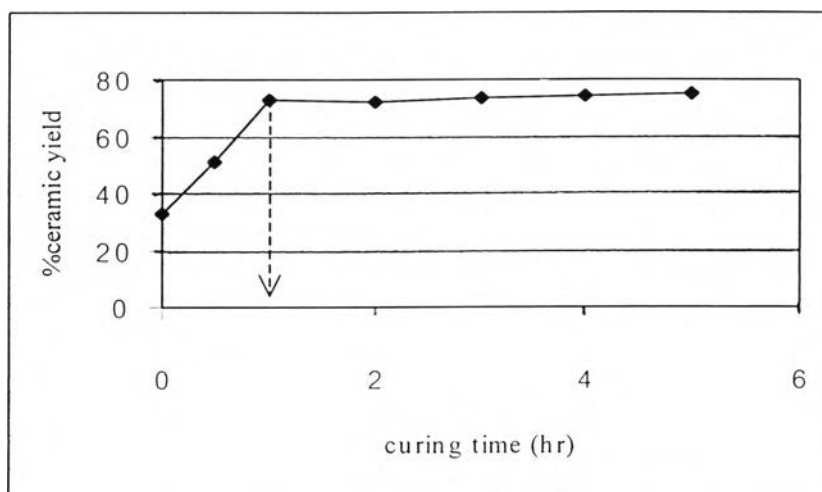
From Figure 4.7, the spirosilicate product was cured by first varying temperature and fixing the time at 1 hr. The %ceramic yield was approaching constant when the temperature reached 120°C under vacuum at 1 torr. This temperature was thus selected to find the optimum time, as can be seen in Figure. 4.8. The curing time studied was ranged from half an hour to 5 hr. It was found that curing time for 1 hr gave the highest %ceramic yield. As a result, the optimum curing condition for the spirosilicate product C2 is 120°C for 1 hr.

As for C3 product. it was cured by varying temperature from 80° to 180°C and fixing the time at 1 hr in vacuum oven. The data reported in Figure. 4.9 shows that the optimum curing temperature at 1 hr curing time was 140 °C owing to the highest %ceramic yield resulted. Thus 140 °C was used to study the curing time by varying the time from half an hour to 5 hr, as shown in Figure. 4.10.
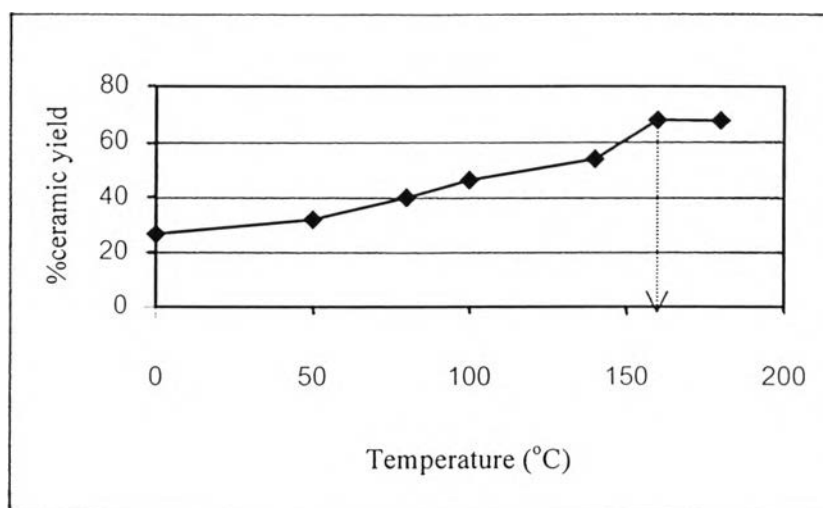

Figure 4.9 Relationship between curing temperature and %ceramic yield of aminospirosilicate C3 product.

From this graph, the line started to approach constant at 1 hr. From the results, the optimum condition for curing C3 product is at 140°C for 1 hr.

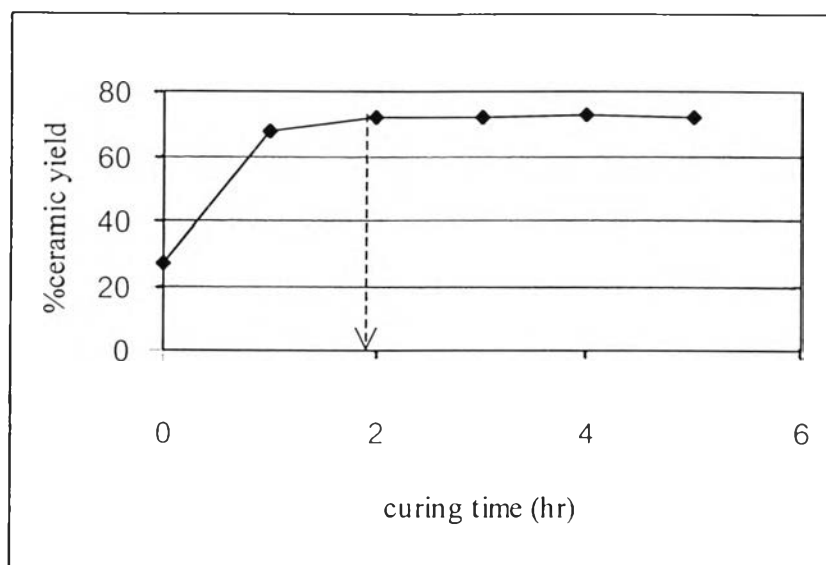**Figure 4.10** Relationship between curing time and %ceramic yield of aminospirosilicate C3 product.

Similarly, the optimum curing condition of C4 aminospirosilicate product was carried out in the same manner. The curing temperature was first studied by varying from 80° to 180°C, and fixing the time at 1 hr. The data were presented in Figure 4.11.

Figure 4.11 Relationship between curing temperature and %ceramic yield
of aminospirosilicate C4 product.

It was found that the temperature resulting in the highest %ceramic
yield was 160°C. The next step was to study the effect of curing time by
varying the time from 1 to 5 hr at the fixed temperature of 160°C, and data
was reported in Figure 4.12. The highest %ceramic yield obtained was at 2
hr. That is, the optimum condition for curing C4 product is at 160°C, 2 hr.

The overall optimum conditions for curing spirosilicate and
aminospirosilicate products are summarized in Table 4.3. From the Table,
aminospirosilicate C4 product uses higher temperature and longer time for
curing the product as compared to C2 and C3 due to the fact that stability of
six- membered ring structure of C4 is higher than those of five-membered
ring C2 and C3.

Figure 4.12 Relationship between curing time and %ceramic yield of
aminospirosilicate C4 product.

Table 4.3 The optimum temperature and time for curing synthesized products.

Product	Temperature (°C)	Time (hr)
C2	120	1
C3	140	1
C4	160	2

4.3 Volumetric Study

After curing the purified products, the volumetric change of polymers as compared to their corresponding monomers were studied using 25 ml pycnometer and distilled isooctane as a media at 25°C. The density property was calculated from the experiment as seen in Appendix II. And the results are shown in the Table 4.4.

Table 4.4 The volumetric property of spirosilicate C2, aminospirosilicate C3   and aminospirosilicate C4 products.

| Product	Density (g/cm^3) *		Result (%)**
	Monomer	**Polymer**	
C2	1.7342	1.7517	-1.01
C3	1.6111	1.6329	-1.35
C4	1.5537	1.5638	-0.65

** (-) Shrinkage ; (+) Expansion

* The data was averaged from 2 or 3 repeatedly experimental values.

From the results, all materials have shown small amount of volumetric shrinkage property. What is the factor that causes the products to shrink?

Cairn (1965) studied the hydrogen bonding in phenol structure and found that Infrared spectroscopy (FTIR) technique can distinguish between inter- and intramolecular hydrogen bonding. As can be seen in the Figure 4.13a, the spectrum of methylamine based dimers showed a sharp peak at 3614 cm^{-1} which is belong to free OH and the broad band at 3380 cm^{-1} assigned to OH--O stretching of intermolecular hydrogen bonding. In the case of novolak's structure, Figure 4.13b, the band at 3476 cm^{-1} was assigned to intramolecular hydrogen bonding. The presence of free hydroxyl group was appeared at 3611 cm^{-1}, and the broad band at 3350 cm^{-1}was belonging to the intermolecular hydrogen bonding.
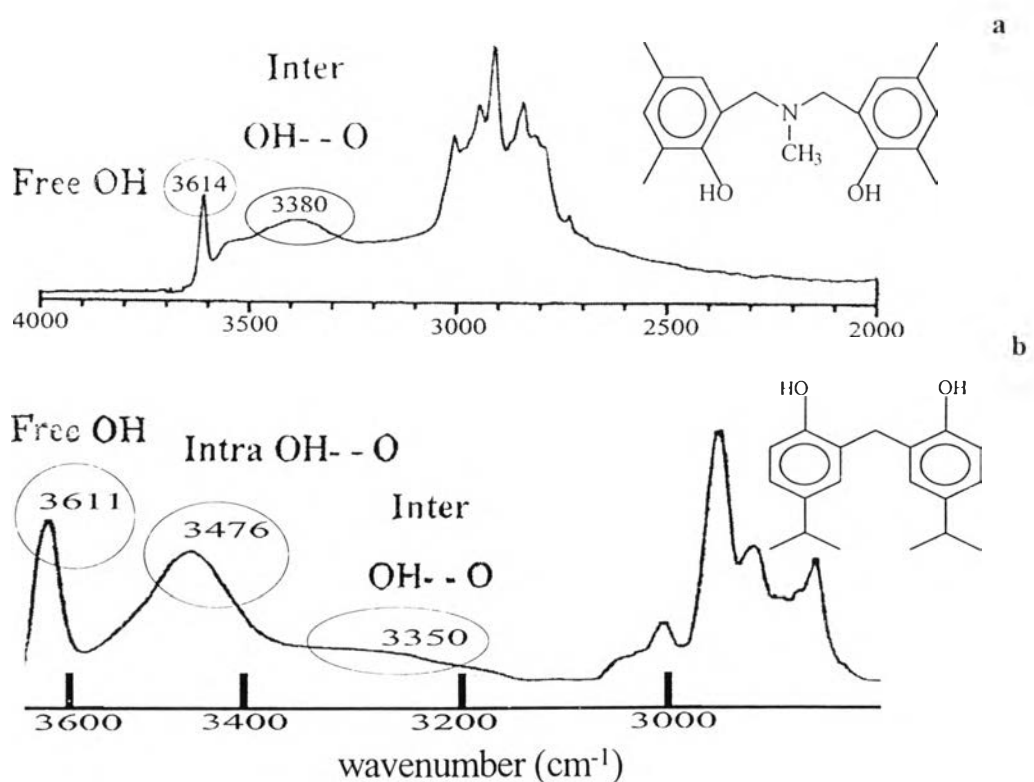

Figure 4.13 FTIR spectra of a) Methylamine based dimers and b) Novolak. (Cairn, T., Eglinton, G , Journal of Chemical Society, **1965**, 5906-5913.)

It can be concluded in Table 4.5 that free hydroxyl group appears as a sharp peak around 3600 cm^{-1}, the intramolecular hydrogen bonding is present as a broad band around 3500 cm^{-1} and intermolecular hydrogen bonding shows a broad band around 3400 cm^{-1}.

Table 4.5 Summarized spectrum band of hydroxyl group by using FTIR technique.

| Type of Hydroxyl group	Position (cm^{-1})
Free Hydroxyl group	Sharp peak around 3600
Intramolecular Hydrogen Bonding	Broad peak around 3500
Intermolecular Hydrogen Bonding	Broad peak around 3400

For the cured products of spirosilicate C2, aminospirosilicates C3 and C4, they showed only broad band at 3403, 3390 and 3405 cm^{-1}, respectively (Figure 4.14). These bands are all assigned to intermolecular hydrogen bonding.

a

b

c
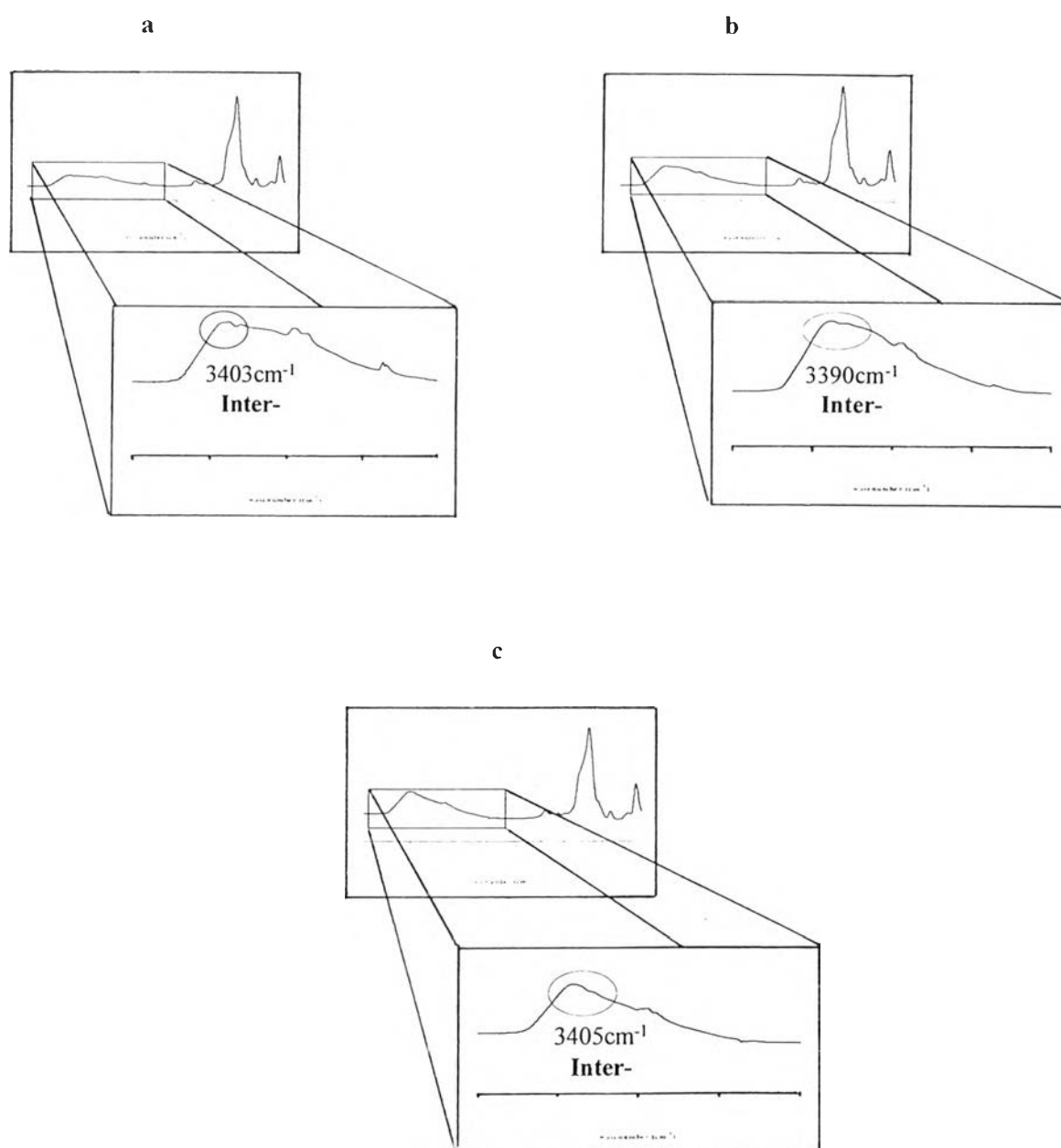
Figure 4.14 FTIR spectra of cured a) spirosilicate C2,

b) aminospirosilicate C3 and c) aminospirosilicate C4 products.

As the results, intermolecular hydrogen bonding (can be seen in Figure 4.15) has significant effect on the volumetric shrinkage property of all products. The more hydrogen bonding in the structure, the higher shrinkage, causing the molecule to come close together (Ishida, 1997).

In the case of C4, due to the steric hindrance in the structure, it has more effect to hydrogen bonding forming, resulting in smaller volumetric change as compared to C2 and C3 products, which C3 has free amino group that can move easily to form hydrogen bonding.
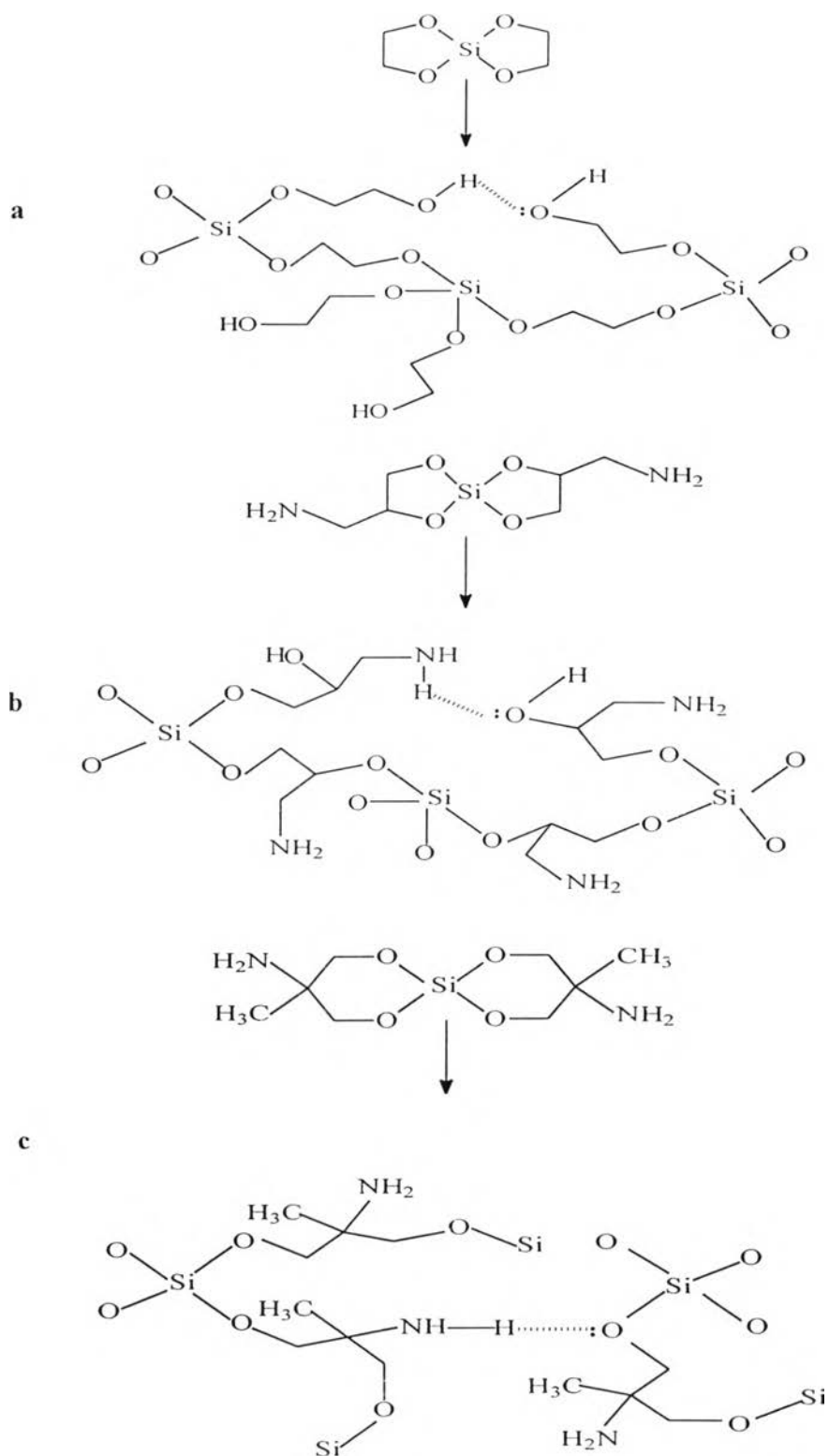
Figure 4.15 Hydrogen bonding occurring in the structure of a) spirosilicate C2, b) aminospirosilicate C3 and c) aminospirosilicate C4.