Chapter IV

Results and Discussion

Selection of Types of Glass and Binder.

The glasses studied in this thesis are borositicate the glass, and soda -lime - silicate glass. They were ground and sieved to required size. Two sizes of borsoilicate, and one size of soda - lime - silicate glass were studied, 180 - 125 μm and 125 - 63 μm for borosilicate glass, and 125 - 63 μm for soda - lime - silicate glass. After the glass powders were prepared, binders were selected. PVA (polyvinyl alcohol) and agar gel were the binders used in this thesis work because they can decay at medium high temperature and can bind the grains of glasses closely. The viscosity of these two glasses at any temperature is shown in the table 4.1, and in figure 4.1.

Table 4.1 The viscosity - temperature relation of borosilicate glass and soda - lime - silicate glass.

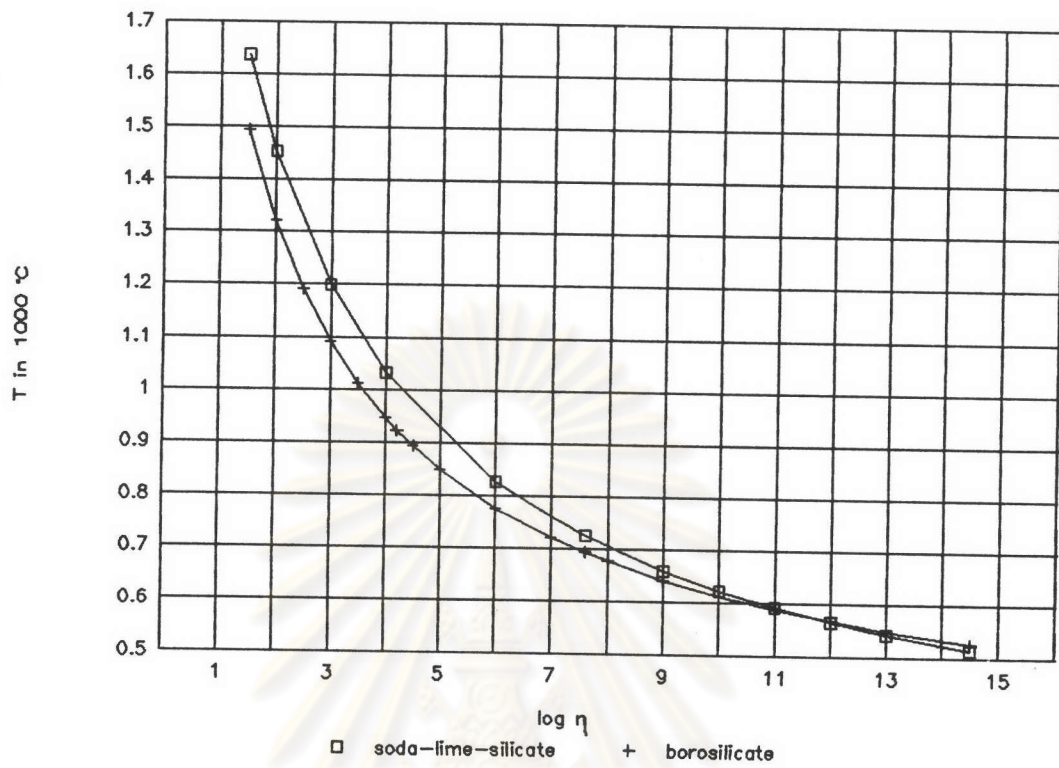| log η	temperature for borosilicate glass (°C)	temperature for soda-lime-silicate glass (°C)
14.5	527.6	514.6
13.0	550.0	543.5
12.0	567.8	566.3
11.0	588.5	592.7
10.0	612.7	623.5
9.0	641.7	660.0
8.0	676.7	-
7.6	693.0	724.1
7.0	720.2	-
6.0	775.4	825.6
5.0	847.8	-
4.5	893.2	-
4.2	922.2	-
4.0	947.1	1031.1
3.5	1011.9	
3.0	1091.5	1197.9
2.5	1191.5	-
2.0	1320.9	1452.5
1.5	1494.9	1637.5

Fig. 4.1 The curves of relation between viscosity and temperature of borosilicate glass and soda-lime-silicate glass.

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Density and Shrinkage of Fired Specimens

After specimens were fired at varying temperatures, T, the density and shrinkage were measured. The result is shown in table 4.2. When T is high, the shrinkage and density are high too. Time is an important factor that influences this result. But in this thesis work, a constant time interval was used because the result of density and shrinkage were compared at varied T. For borosilicate glass size 125 - 63 μm and size 180 - 125 μm, the trend of shrinkage was the same (see figure 4.2), The shrinkage of soda - lime - silicate glass is also plotted in the figure 4.2, and shows the same tend as borosilicate glass. The shrinkage of specimens can be determined from the before - fire - porosity by the formula $d = m/V$ where d is density of the glass before firing, m is its mass of glasses and V is its volume calculated from the formula $V = \pi r^2 h$.

Density of specimens was measured after 3 hours. It shows that when the time was fixed, and only T was varied, the density was increased with T, but at high T, the specimens collapsed. Closely to the Littleton temperature, the specimens nearly reach the standard density of their type.

Table 4.2 Density and shrinkage of specimen after firing for 3 hours at different viscosity levels; standard densities are 2.50 g/cm^3 for borosilicate glass and 2.48 g/cm^3 for soda - lime silicate glass.

Glass	log η	Density	% Shrinkage in length	% Volume Shrinkage
Borosilicate glass size 125 - 63 μm	9.7	2.456	19.5	39.1
	9.4	2.462	20.8	39.4
	8.7	2.463	24.6	39.9
	8.5	2.464	27.6	41.0
	8.2	2.467	28.2	41.9
	7.9	2.469	38.5	43.6
Borosilicate glass size 180 - 125 μm	9.7	2.455	19.1	38.7
	9.4	2.456	20.2	38.7
	8.7	2.462	22.4	41.0
	8.5	2.465	26.8	41.6
	8.2	2.468	28.5	41.7
	7.9	2.469	35.3	42.5
Soda-lime-silicate glass size 125 - 63 μm	10.1	2.220	6.1	18.1
	9.9	2.278	7.6	18.5
	9.3	2.395	18.3	30.5
	9.0	2.424	19.3	38.5
	8.8	2.435	20.4	40.3
	8.6	2.436	23.7	40.8
	8.1	2.437	27.7	41.7
	7.7	2.444	33.8	42.9
	7.4	2.446	44.9	45.4

Closed Porosity

When specimens were fired, especially closely to the Littleton temperature (T(7.6)), the density came closed to the standard density (see table 4.3). The percentage of closed porosity was calculated. It can be shown that even though the specimens were fired at high T, there were remaining voids in the specimen. Closed porosity occured when the grains of glass powders melted to combine each other but they could not reach 100 %. The way to solve that problem is not firing at higher T, but taking longer soaking time to be sure that the porosity will be removed. However, a certain amount of closed porosity cannot be removed even at longer times. The problem lies in the viscous flow itself which traps bubbles in such a way that they cannot escape. Thus, even very long sintering times will not make transparent glass samples. If transparency is the target, then a zone sinter technique has to be applied where the sintering starts from the inner axis of the sample and proceeds to the outside. For the purpose of this thesis, zero open porosity was sufficient.

Calculation of closed porosity is made by using this formula

% closed porosity = 100 - % standard density of glass   4.1

Table 4.3 Density and closed porosity of specimen

Glass	log η	% Standard density	% Closed porosity
Borosilicate glass size 125 - 63 μm	9.7	98.25	1.75
	9.4	98.48	1.52
	8.7	98.51	1.49
	8.5	98.56	1.44
	8.2	98.67	1.33
	7.9	98.76	1.24
Borosilicate glass size 180 - 125 μm	9.7	98.20	1.80
	9.4	98.38	1.62
	8.7	98.48	1.52
	8.5	98.61	1.39
	8.2	98.70	1.30
	7.9	98.74	1.26
Soda-lime-silicate glass size 125 - 63 μm	10.1	91.06	8.10
	9.9	91.86	8.01
	9.3	96.56	3.43
	9.0	97.75	2.25
	8.8	98.18	1.82
	8.6	98.22	1.78
	8.1	98.27	1.73
	7.7	98.58	1.42
	7.4	98.64	1.36

Table 4.4 Open porosity of specimen at high n.n.

Sample No.	Glass	log η	% Open porosity
1	Soda-lime-silicate glass size 125 - 63 μm	10.1	0.16
1 2 3	Soda-lime-silicate glass size 125 - 63 μm	9.9	0.11 0.14 0.13
1 2 3	Soda-lime-silicate glass size 125 - 63 μm	9.3	< 0.01 < 0.01 < 0.01

Fig. 4.2 Comparison of density and log η between borosilicate glass, and soda-lime-silicate glass.

Remark : JM is borosilicate glass

CMG is soda-lime-silicate glass

Shrinkage Curves from the Long-Range Dilatometer

When the new dilatometer was applied in the experiments, the heating rate of the dilatometer furnace and the voltage from the distance sensor were measured by a computer. When the shrinkage of sample was measure from room temperature to $T(5.6)$ for borosilicate glass and to $T(6.0)$ for soda - lime - silicate glass, the heating rate was 5 K/min to be sured that the shrinkage can follow the heating rate.

It can be observed that the shrinkage of specimen measured in the new dilatometer was higher than the shrinkage of specimens fired in the annealing furnace. This is because in the dilatometer furnace, the shrinkage was measured in vertical position with the weight of the silica rod and the iron plate pressed on the top of samples. Without any counter measured, the load was 55 g. That made the specimens shrinkage was much more than when firing in the annealing furnace where were placed on a support only (table 4.5). To avoid the effect of assistant pressure, a spring with a proper spring constant was applied to reduce the force pressing on the specimens to 5 - 10 g. There was a little force that made the specimens have more shrinkage.

The heating characteristics of the dilatometer furnace is shown in figure 4.3. It shows the good efficiency of the furnace because the desired heating rate can be verified.

The further studies on the shrinkage of specimens were the shrinkage curve at a pre - set viscosity level, $T(n.n)$, with the soaking time being the parameter. Prior to inserting the specimen, the furnace was heated up to the desired level at a heating rate of 10 K/min. Figure 4.4 gives an example. So, shrinkage was not measured from room temperature, but
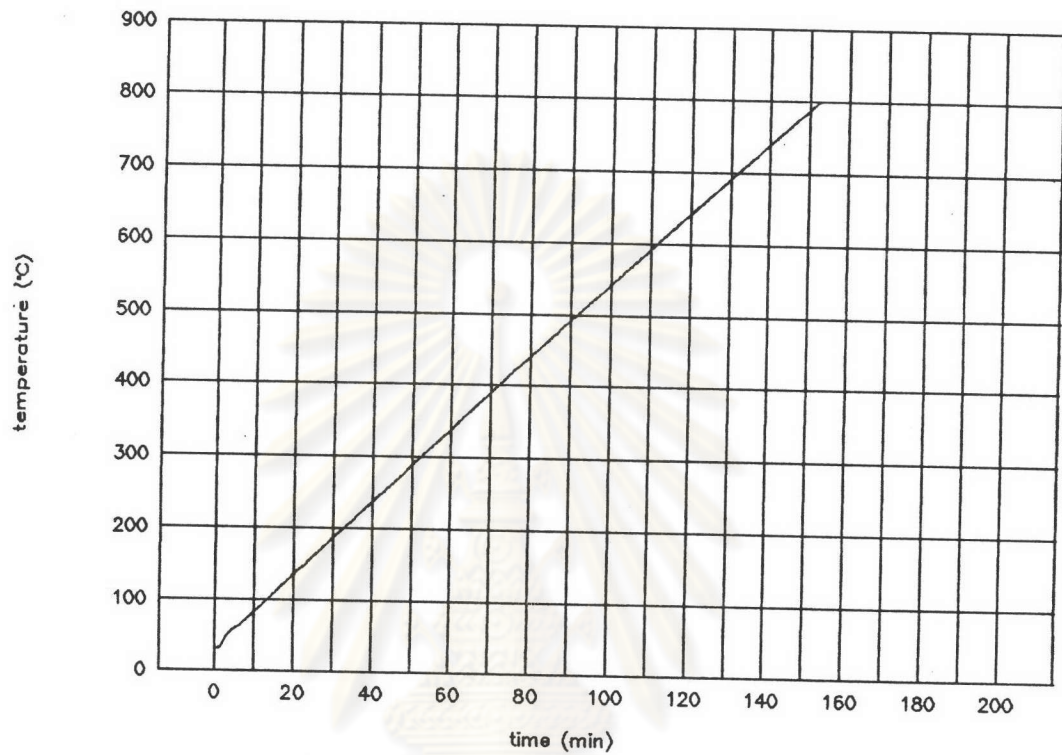
Fig. 4.3 Heating curve of dilatometer furnace from room temperature
to 800 °C at heating rate 5 K/min.

Table 4.5 Comparison between the shrinkage of specimen fired in annealing furnace and in the dilatometer furnace.

Glass	T(n.n)	% Shrinkage in the annealing furnace	% Shrinkage in the dilatometer furnace
Borosilicate glass	T(8.5)	26.8	40.5
Soda-lime-silicate glass	T(8.6)	23.7	38.7
	T(8.1)	27.7	42.4

measurement started at T(n.n). The shrinkage in this case is very close to situation when the specimens were put into the hot dilatometer furnace.

Test of borosilicate glass specimens: The borosilicate glass specimen was tested at T(8.5) (figure 4.5). The size used in this case is 125 - 63 µm because it can be compared with soda - lime - silicate glass specimens prepared with the same size (figures 4.6 and 4.7). It shows that the trend of shrikage of those is the same that is there is a fast shrinkage in the begining and then the shrinking rate slows down. The porosity of these samples prior to firing were different, thus the final shrinkage shown in the figure is also not the same. The reason for the fluctuation of initial porosity is seen in the use of the pellet press. This machine is operated by human force. So the pressing force could not be controlled well. The calculated porosity before firing of borosilicate and soda - lime - silicate glass specimens is shown in table 4.6.

Table 4.6   The porosity of borosilicate and soda - lime - silicate glass specimens before firing used in finding shrinkage curve at constant T(n.n); the standard densitis are 2.50 g/cm^3 for borosilicate glass and 2.48 g/cm^3 for soda - lime - silicate glass.

Sample	Density (g/cm^3)	% Porosity before firing	%Standard density
1. Borosilicate glass for T(8.5)	1.446	42.17	57.83
2. Soda-lime-silicate glass for T(8.6)	1.410	43.14	56.86
3. Soda-lime-silicate glass for T(8.1)	1.393	43.82	56.18

specimen exposed to
the furnace
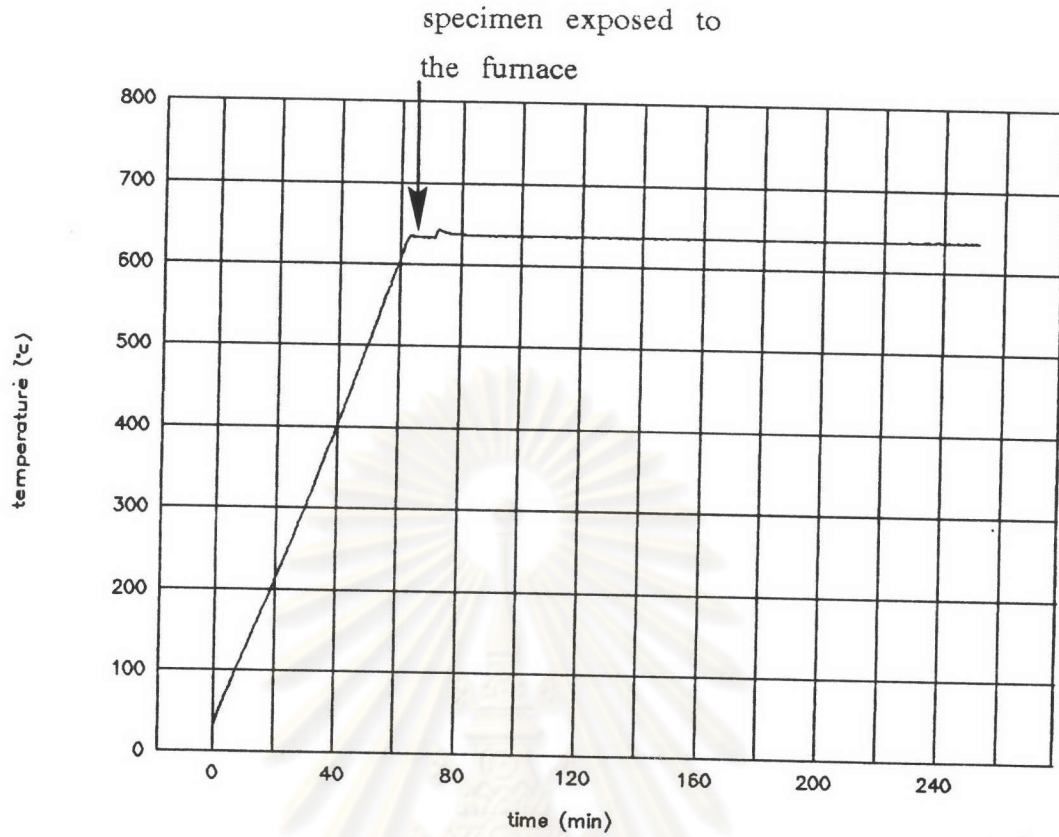
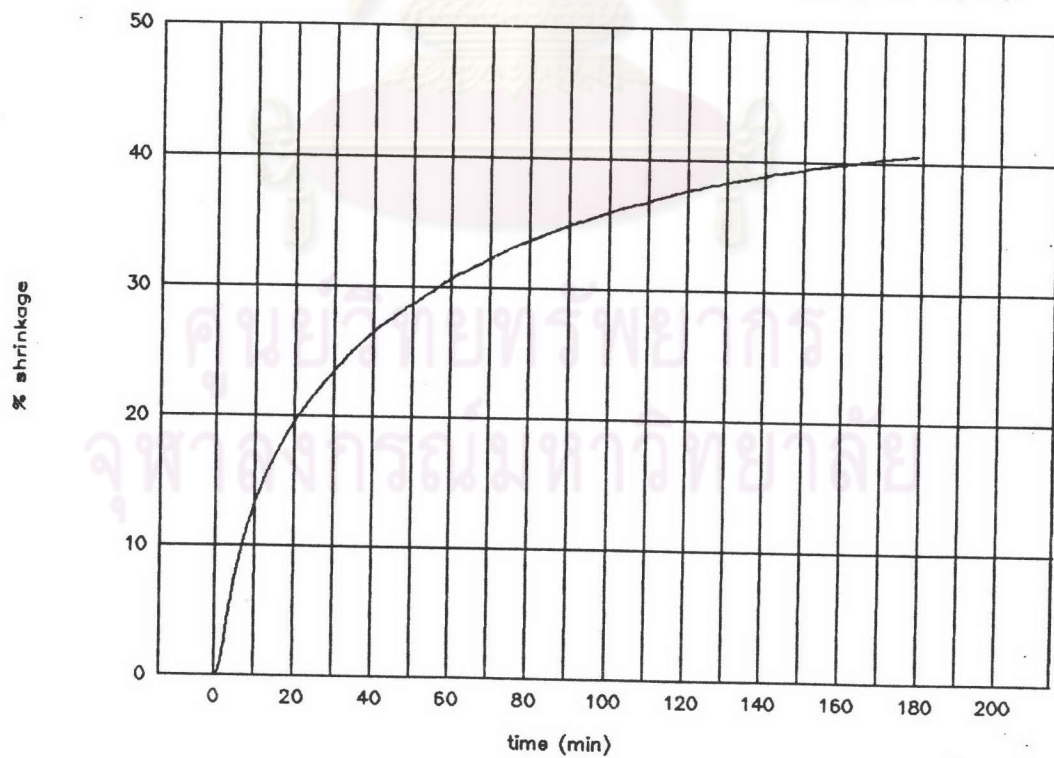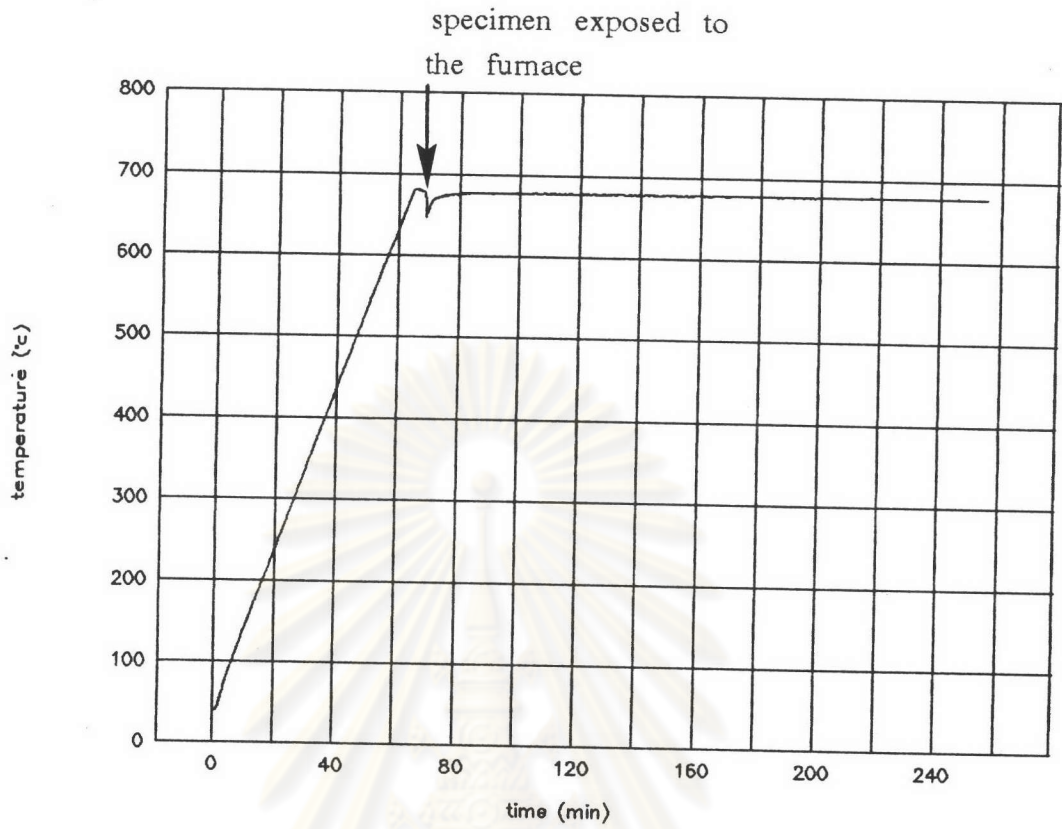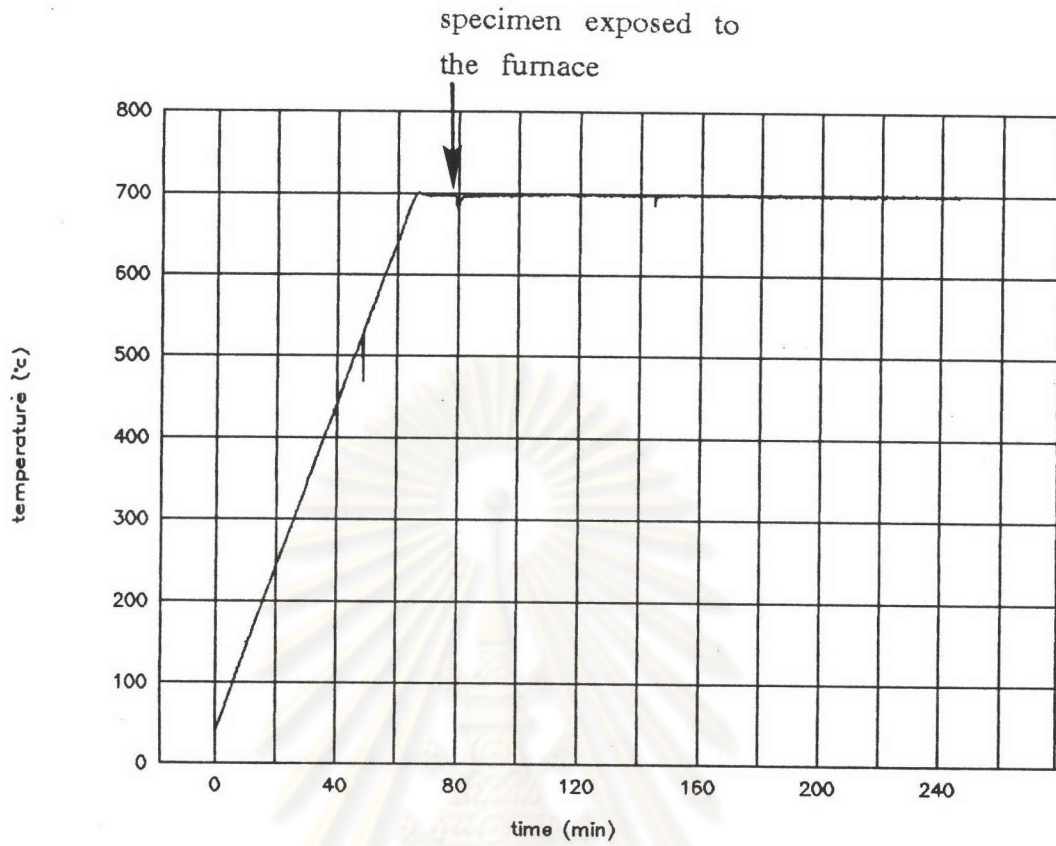Fig. 4.4 Temperature heat up for dilatometer when loading at T(8.5).

Fig. 4.5 Shrinkage curve for borosilicate glass size 125 - 63 μm at T(8.5)
for 3 hours.

The test of soda - lime - silicate glass specimens at T(8.1) (figures 4.8 and 4.9) shows the tendency as described above. The curves will be evaluated quantitatively in chapter 4.2.

specimen exposed to
the furnace

Fig. 4.6   Temperature heat up for dilatometer when loading at T(8.6).
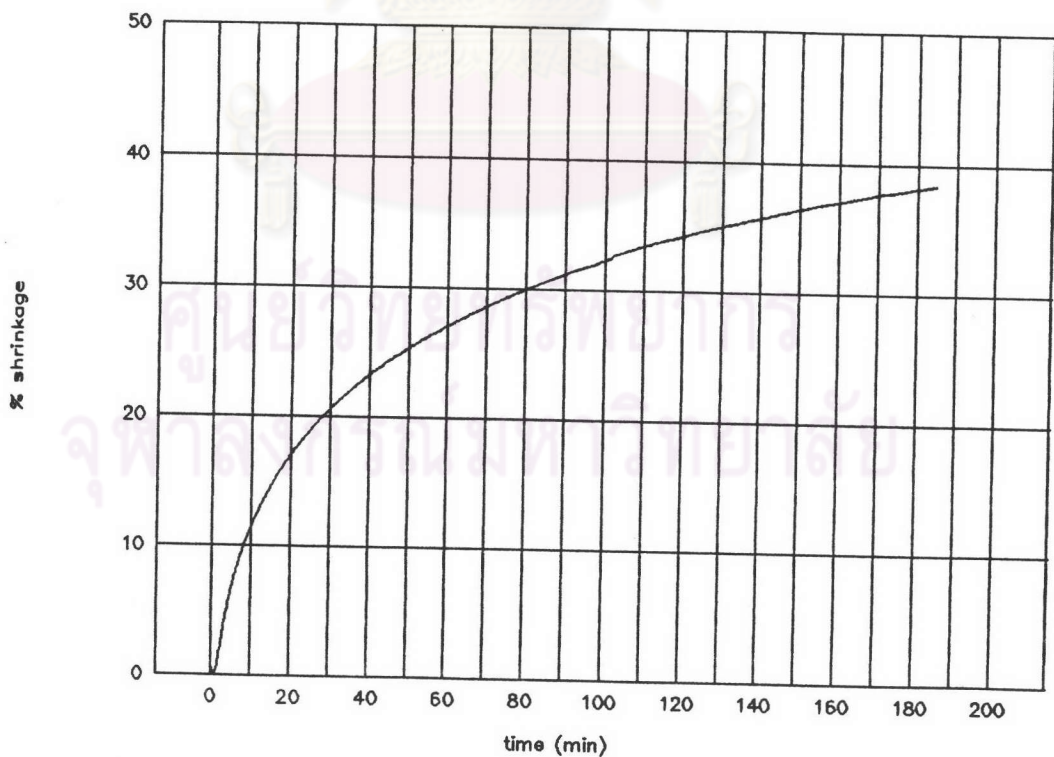
Fig. 4.7   Shrinkage curve for soda - lime - silicate glass size 125 - 63 µm at
T(8.6) for 3 hours.

specimen exposed to
the furnace

Fig. 4.8   Temperature heat up for dilatometer when loading at T(8.1).
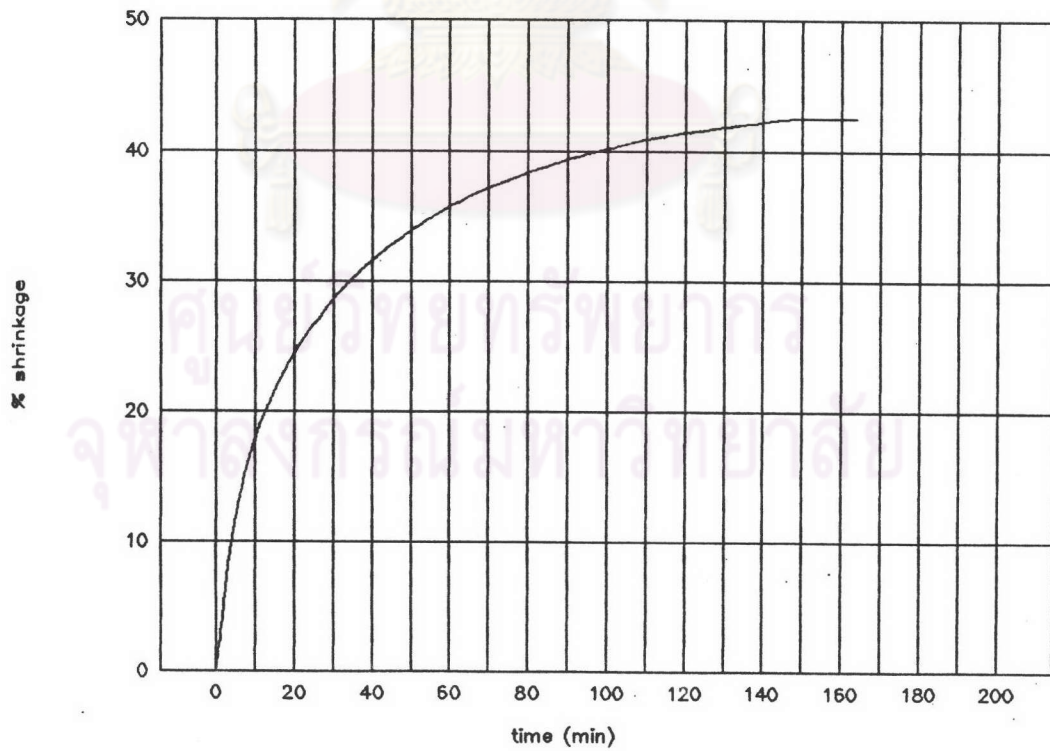
Fig. 4.9   Shrinkage curve for soda - lime - silicate glass size 125 - 63 μm at
T(8.1) for 3 hours.

Sintering Kinetics

4.1 Viscosity Shrinkage

The shrinkage curves recorded on - line from specimen heated up at a constant heating rate of 5 K/min are shown in figures 4.10 to 4.12. Instead of the temperatures, the corresponding log η values are chosen as abscissa. The importance of using viscosity instead of temperature stems from the equation 2.1 on page 15.

These figures show the relation of log η and % shrinkage of the specimens from room temperature to T(5.6) for borosilicate glass and to T(6.1) for soda-lime-silicate glass. These can determine the start and the final of sintering of specimens by extrapolating the curves from ranges of constant slope as sketched in figure 4.1. Borosilicate glass size 125 - 63 μm started sintering at T(9.0) and finished at T(6.8), in the same way, start and finish of sintering for borolilicate size 180 - 125 μm and soda-lime-silicate glass size 125 - 63 μm can be determined also. Borosilicate glass size 180 - 125 μm started sintering at T(8.7) and finished at T(6.8), and soda-lime-silicate glass started at T(8.8) and finished at T(6.7). The result of start and finish of sintering are shown in table 4.6.
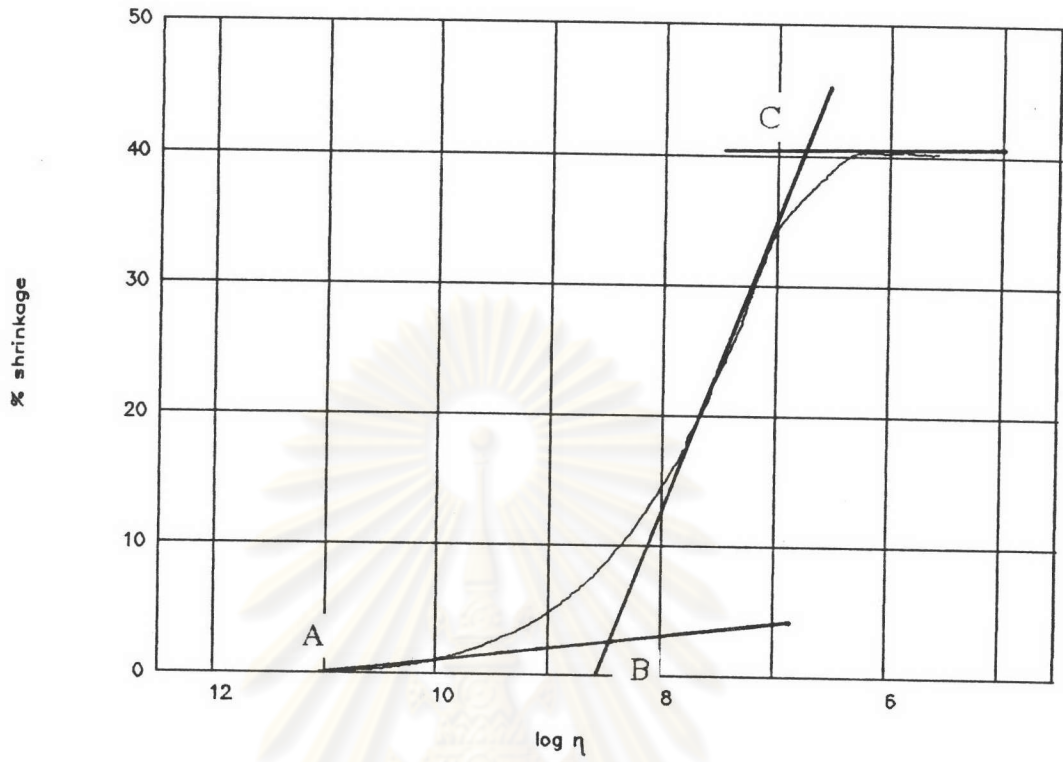
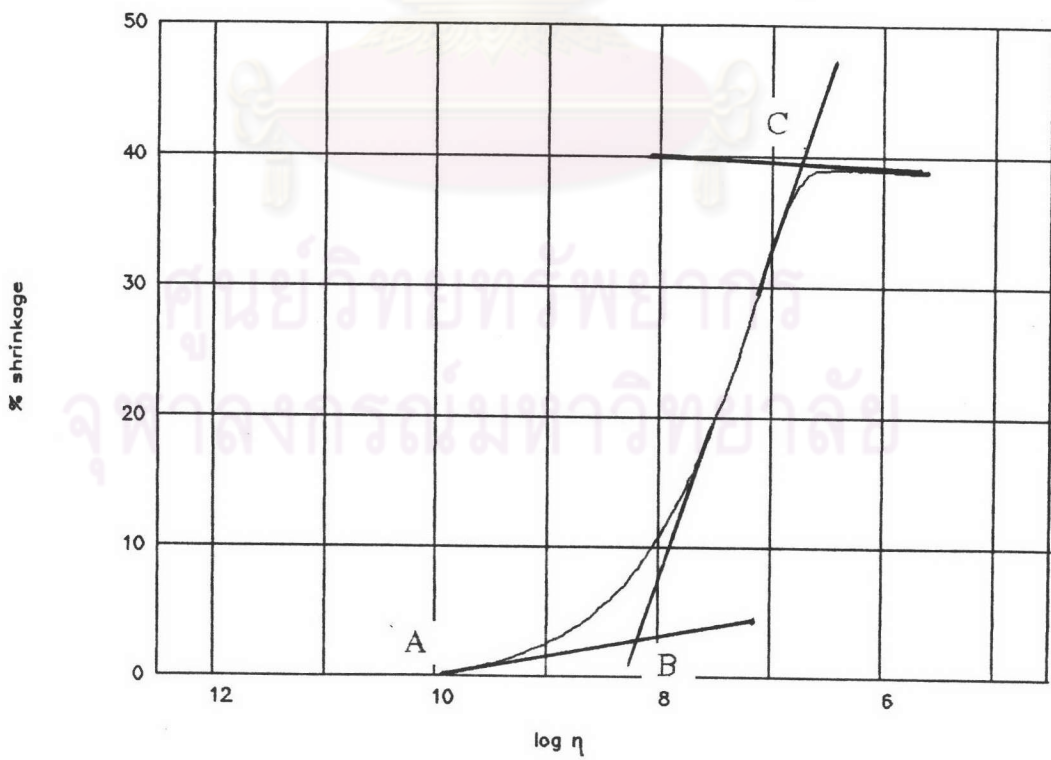Fig. 4.10 Shrinkage curve for borosilicate glass size 125 - 63 μm

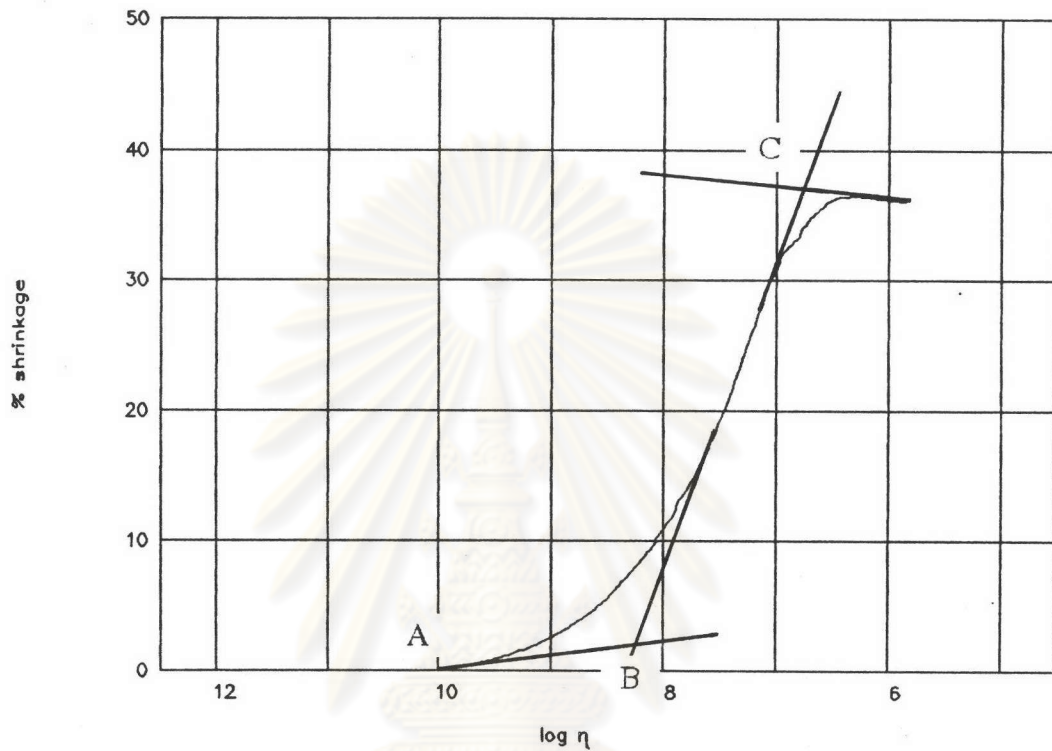·Fig. 4.11 Shrinkage curve for borosilicate glass size 180 - 125 μm

Fig. 4.12 Shrinkage curve for soda - lime - silicate glass size 125 - 63 μm.

Table 4.7 Start and finish sintering of borosilicate glass and soda - lime - silicate glass

Glass	A	B	C
Borosilicate glass size 125 - 63 μm	10.8	8.4	6.8
Borosilicate glass size 180 - 125 μm	9.9	8.2	6.8
Soda - lime - silicate glass size 125 - 63 μm	10.0	8.2	6.8

4.2 Time Law

The data from the sinter tests at constant temperature level (figures 4.5, 4.7, and 4.9) are evaluated quantitatively. Results are shown in figure 4.13 for borosilicate glass and figure 4.14 and 4.15 for soda-lime-silicate glass. The kinetics of these glasses can be calculated to fit the curves. Firstly, an exponential kinetics was tried plotting $\ln[(S_\infty - S)/S_\infty]$ versus t. The normalized shrinkage here as a function of time, S_t, is given by

$$S_t = (S_\infty - S) / S_\infty \; ; \qquad\qquad 4.2$$

S_∞ is % porosity of glass before firing equal to the most shrinkage.

S is unnormalized shrinkage at time t.

Then the following formula 4.3 is applied to perform a regression analysis of the shrinkage:

$$\ln S_t = \ln (S_\infty - S) / S_\infty = \ln S_0 - t/\tau \qquad\qquad 4.3$$

while S_0 is initial shrinkage

τ is a characteristic relaxation time in min

t is time in min

But the exponential kinetics did not fit the data well. So an Avrami - Erofe'ev type is used to analyze the shrinkage curve at different temperatures. The equation used is

$$\ln(-\ln(S_\infty - S)/S_\infty) = N \ln t - N \ln \tau \qquad\qquad 4.4$$

with slope N and intercept $N\ln \tau$

From Avrami - Erofe'ev type, the shrinkage at any time can be calculated from the equation.

$$S_{cal} = S_{\infty} [1 - \exp -(t/\tau)^N]$$ 4.5

From this equation the S_{cal} can be found and fit the shrinkage curves shown in figure 4.13 for borosilicate glass, and figure 4.14 and 4.15 for soda-lime-silicate glass. The agreement is very good.

The equation can also be used to calculate the time demand, t_{xy}, to reach xy % of the standard density. It is given by

$$t_{xy} = \tau [-\ln (1 - 0.xy)^{1/N}]$$ 4.6

where x, and y are any numbers

The value of N, τ, t_{50}, t_{90}, t_{95} for the two glasses at different sintering temperature were calculated and shown in the table 4.7.

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Table 4.8 The calculated values of N, τ, t_{50}, t_{90}, t_{95} of these glasses

Condition	τ	N	t_{50} (min)	t_{90} (min)	t_{95} (min)
Borosilicate glass fired at T(8.5)	40.2	0.74	38	125	163
Soda-lime-silicate glass fired at T(8.6)	59.4	0.66	63	208	270
Soda-lime-silicate glass fired at T(8.1)	27.6	0.71	27	90	117

For comparison of the shrinkage curve of samples, the shrinkage is presented in a normalized scale, i.e., normalized to 100 % final shrinkage. The curves are shown in the figure 4.16 for borosilicate glass and 4.17 for soda - lime - silicate glass.
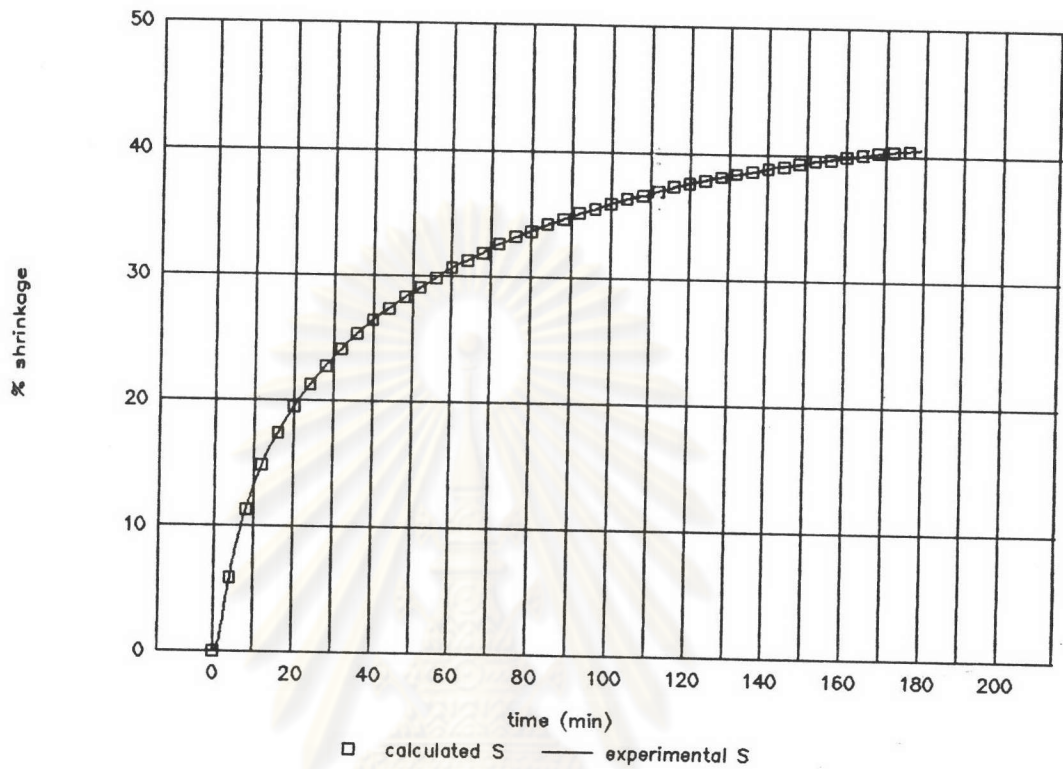
Fig. 4.13 Calculated shrinkage fitting for shrinkage curve of borosilicate glass at T(8.5)
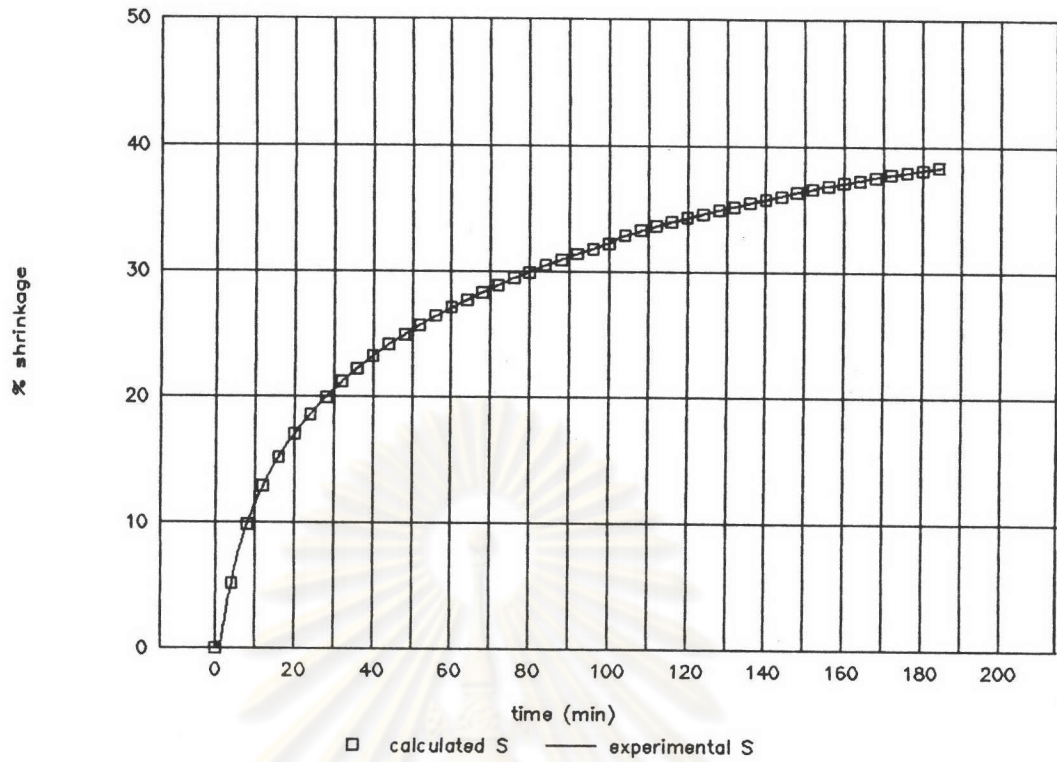
Fig. 4.14 Calculated shrinkage fitting for shrinkage curve of soda - lime - silicate glass   at T(8.6)
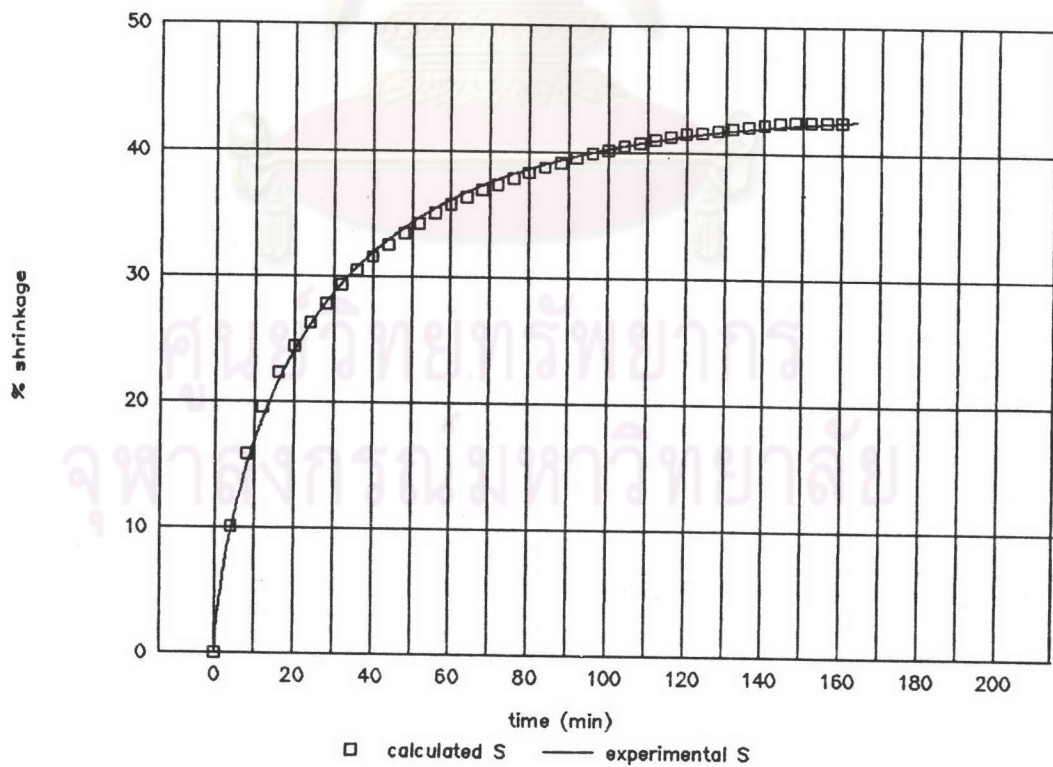
Fig. 4.15 Calculated shrinkage fitting for shrinkage curve of soda - lime - silicate glass at T(8.1)
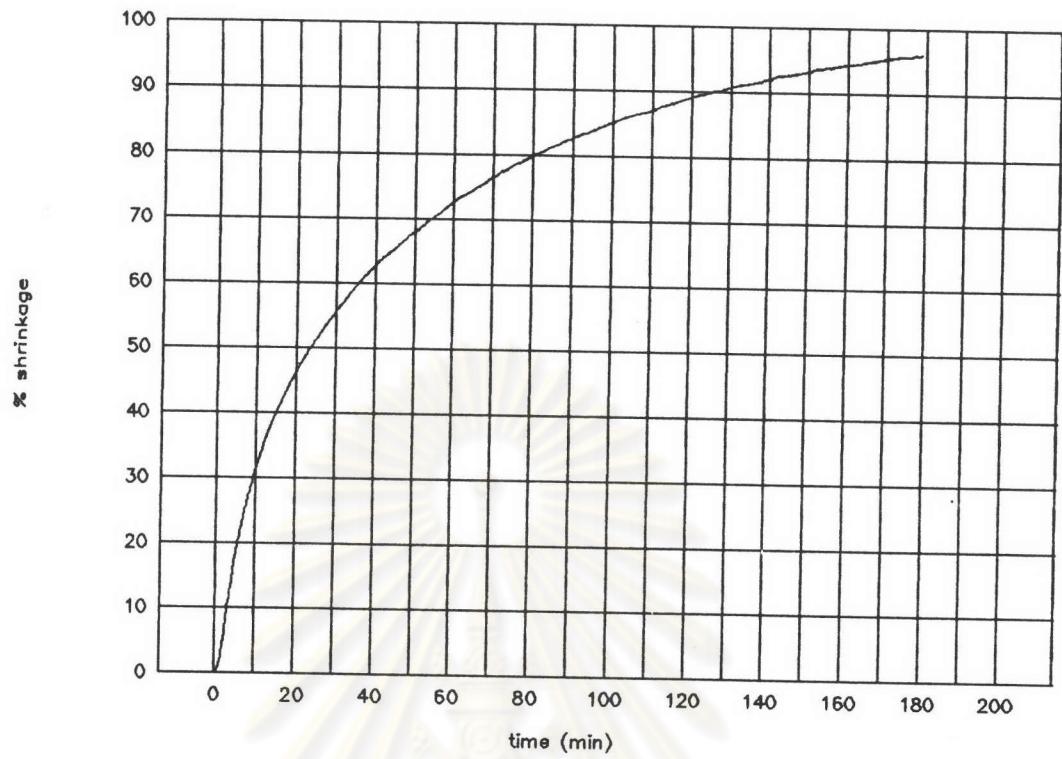
Fig. 4.16 Shrinkage curve of borosilicate glass normalized to 100 %
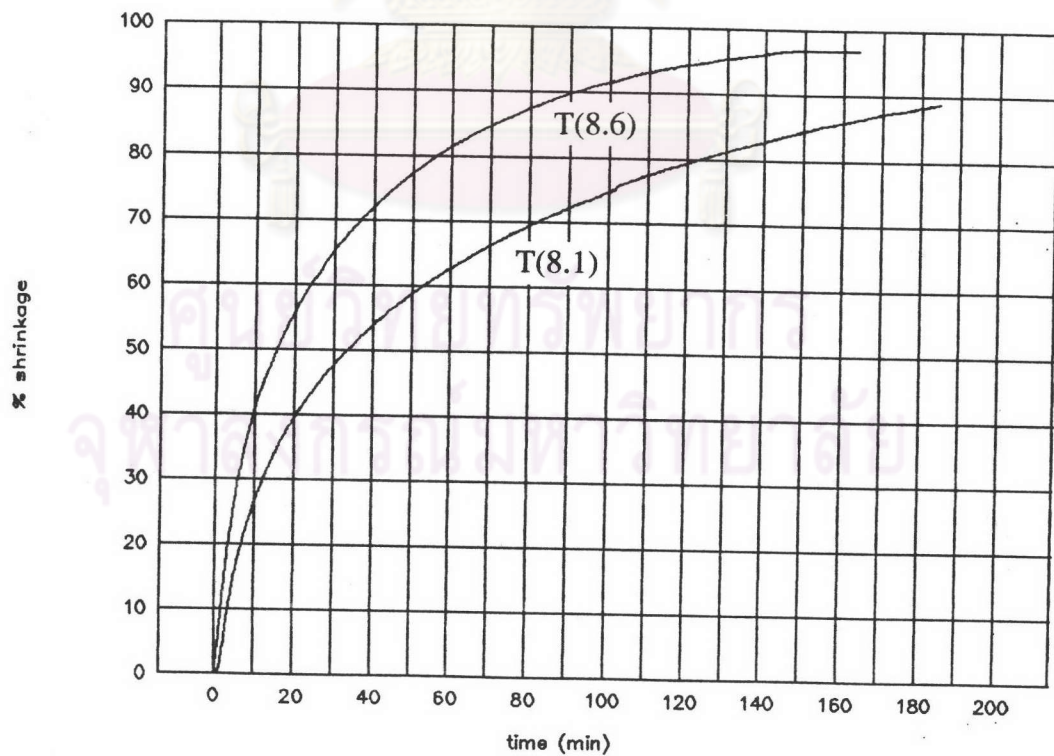shrinkage at T(8.5)

Fig. 4.17 Shrinkage curve of soda - lime - silicate glass normalized to 100 %
shrinkage at T(8.6) and T(8.1)

Microstructure of Fired Specimens

After firing, the microstructure of the specimens was observed by SEM (JEOL 35CF), by a magnification of 800 x and 20 kV of electron beam energy. The microstructures of borocilicate glass and soda - lime - silicate glass shows the same trend. Borocilicate glass, for both sizes 125 - 63 μm and 180 - 125 μm, were observed after firing at T(9.7) and T(7.9). Soda - lime - silicate glass was investigated on 3 samples. These are the samples fired at T(10.1), T(9.0), and T(7.7). The microstructure of these samples shows that there was no obvious viscous flow at low T, but viscous flow was visible for high T. For borosilicate glass, there is a little bit grain that cannot flow together at T(9.7), but the sintering is quite complet when fired at T(7.9). In the same way, the grain of glass powders of soda - lime - silicate glass can be seen clearly in the sample fired at T(10.1). The pore size of this specimen is 50 - 100 μm, and the sintering of this sample is going better when fired at high T. The sintering was complete at T(7.7).

The particles of the initial glass powder is seen in the SEM micrograph in the figure 4.18 for borsicate glass size 125 - 63 μm, figure 4.19 for borosilicate glass size 180 - 125 μm, and figure 4.20 for soda - lime - silicate glass. These show that the shape of particle is not a sphereical, but had the typical of irregularly broken particles.
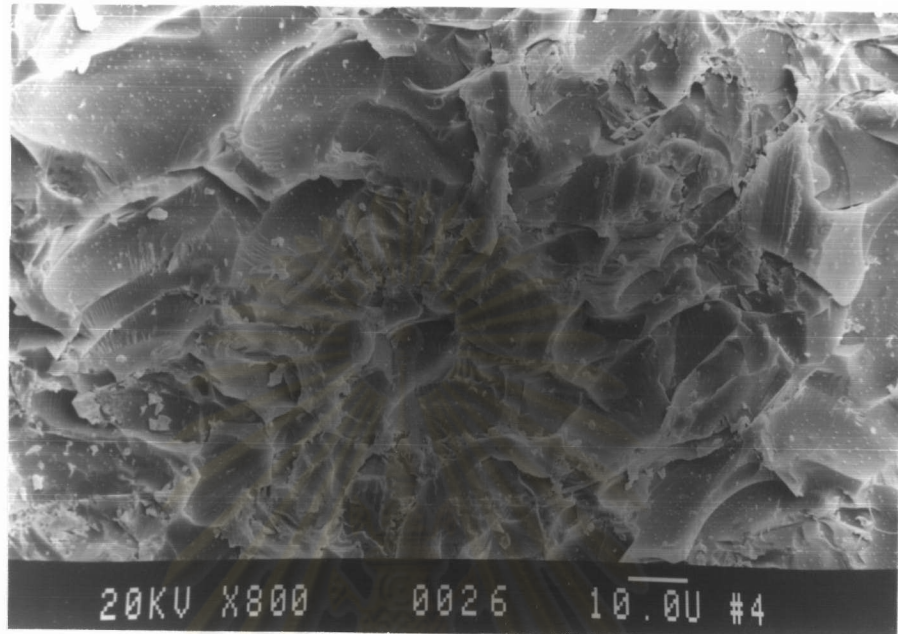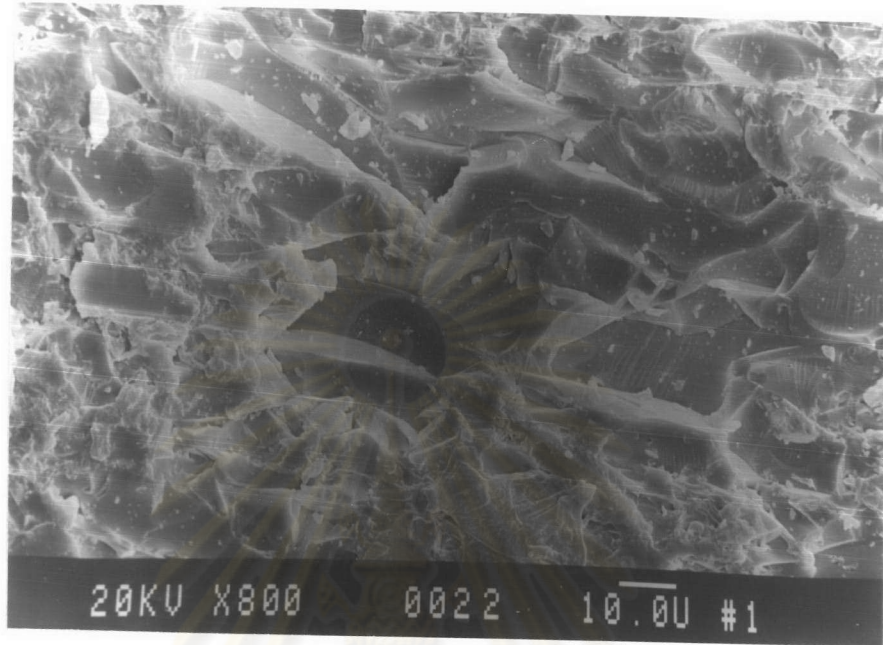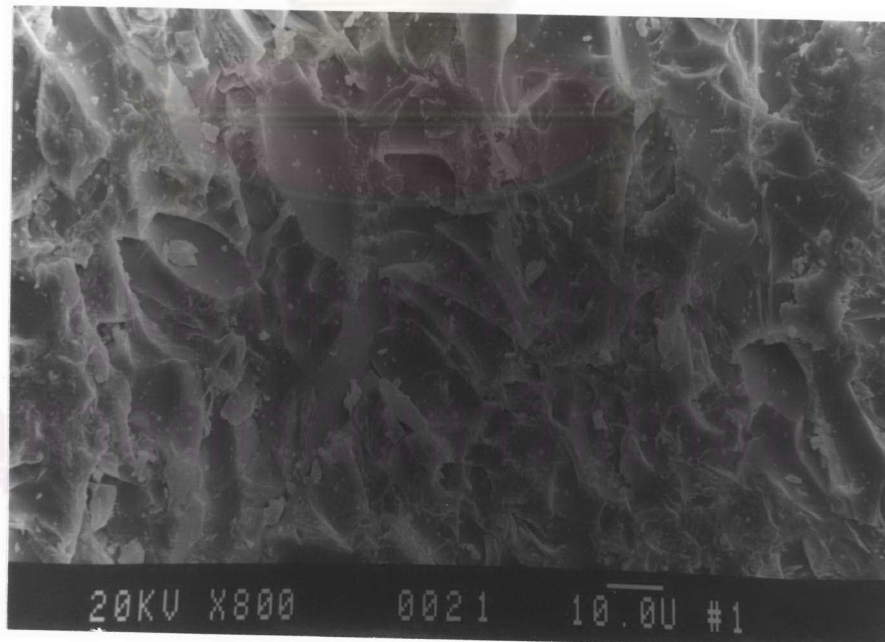
(a)
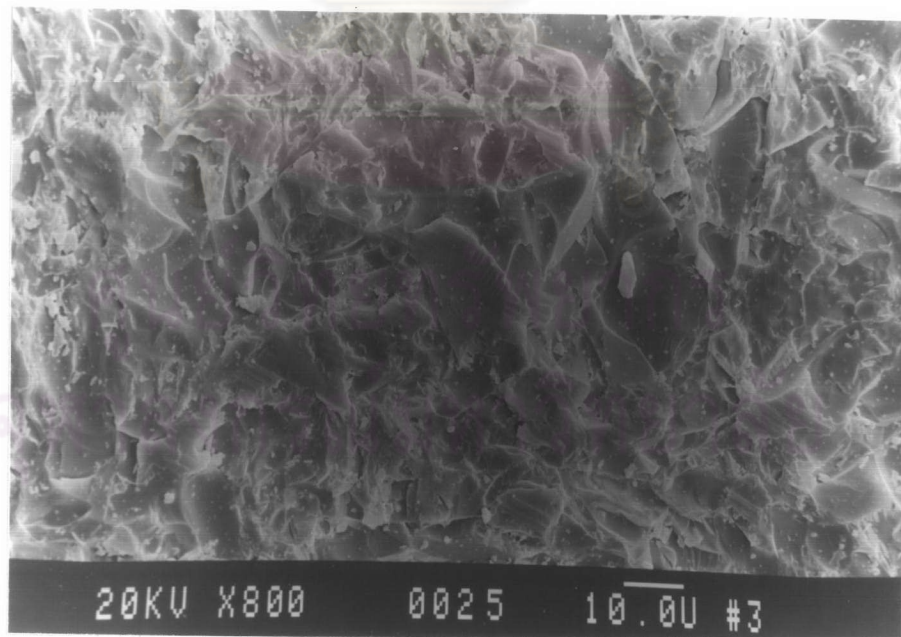
(b)

Fig. 4.18 Microstructure of borosilicate glass size 125 - 63 μm after firing at
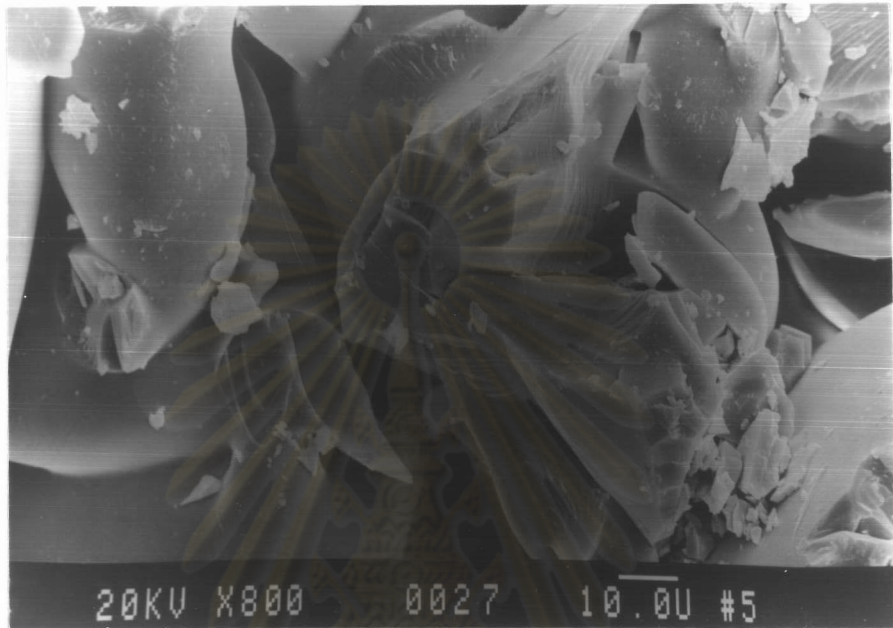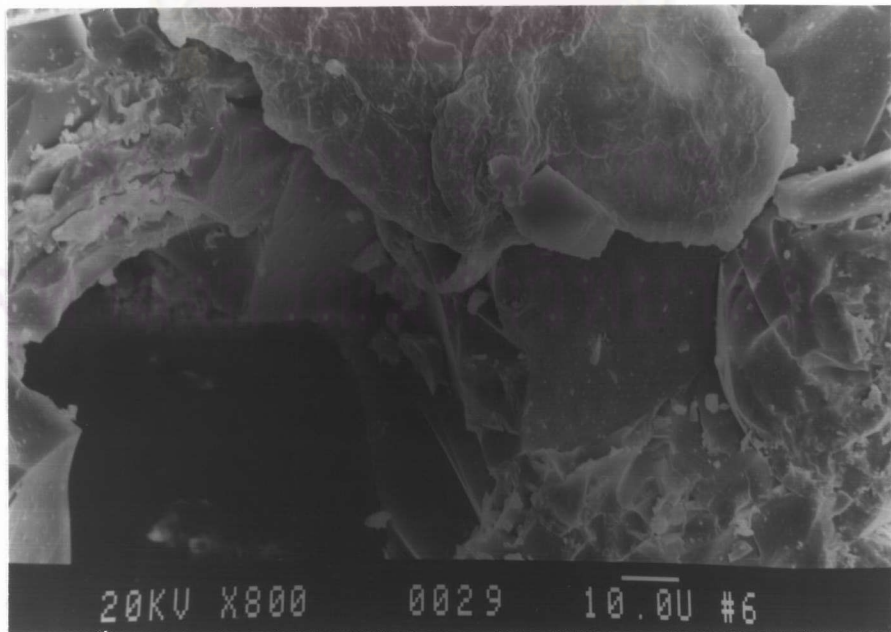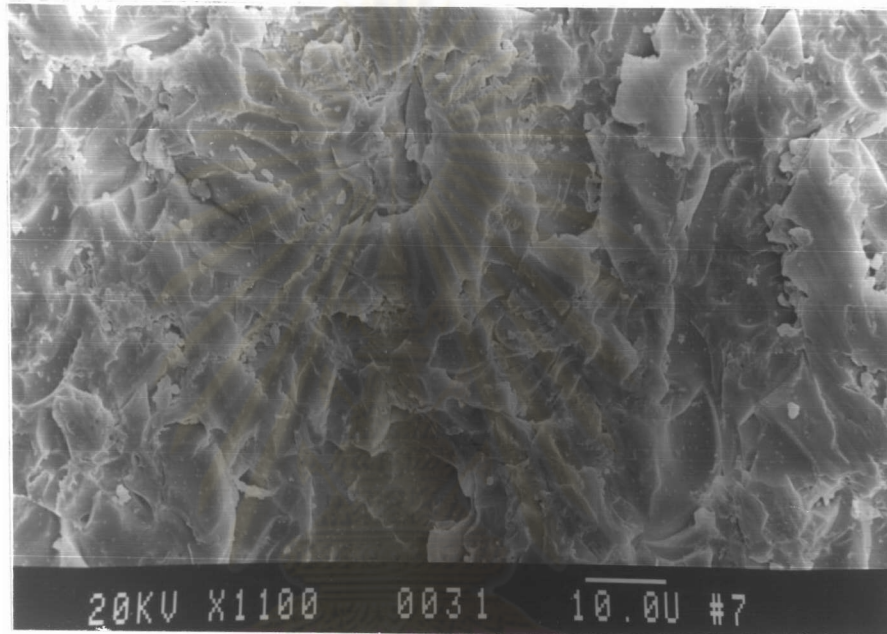(a) T(9.7), and (b) T(7.9)

(a)

(b)

Fig. 4.19 Microstructure of borosilicate glass size 180 - 125 μm after firing at (a) T(9.7), and (b) T(7.9)

20KV X800   0027   10.0U #5

(a)

20KV X800   0029   10.0U #6

(b)

(c)

Fig. 4.20 Microstructure of soda-lime-silicate glass size 125 - 63 µm after firing at (a) T (9.9), (b) T(9.0), and (c) T(7.7)