

Chapter 3

Experimental Part

3.1 Description of Experiments

A starting of experiment was to choose the interesting glass compositions from the phase diagram CaO-P₂O₅ system (in Figure 3-1). After that the experiment was classified into 5 steps: starting material preparation, glass preparation, study on nucleation and crystallization by DTA, study on viscosity by drop test method and fiber formation . All of the experiment sequences were illustrated in Figure 3-2.

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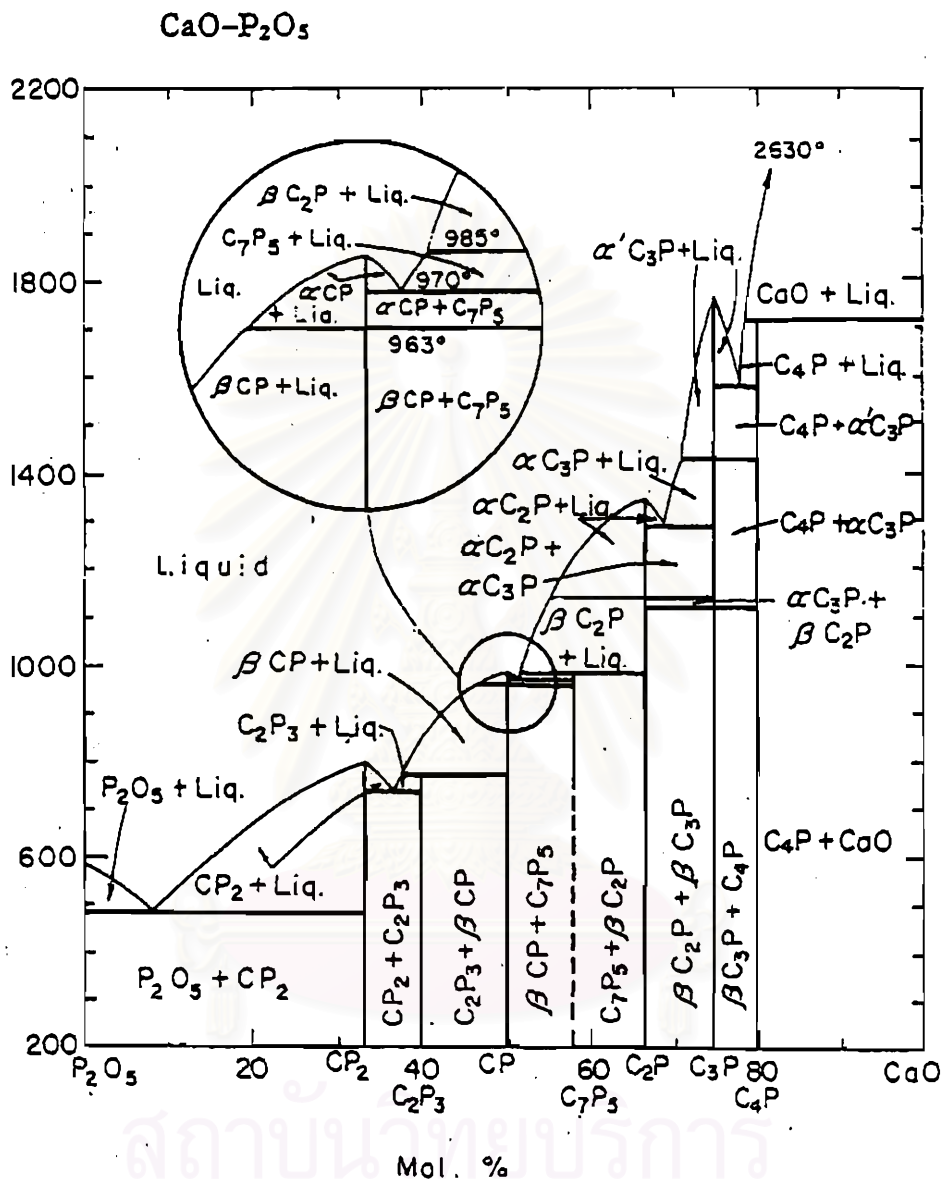


Figure 3-1 Phase diagram of CaO:P₂O₅ system.

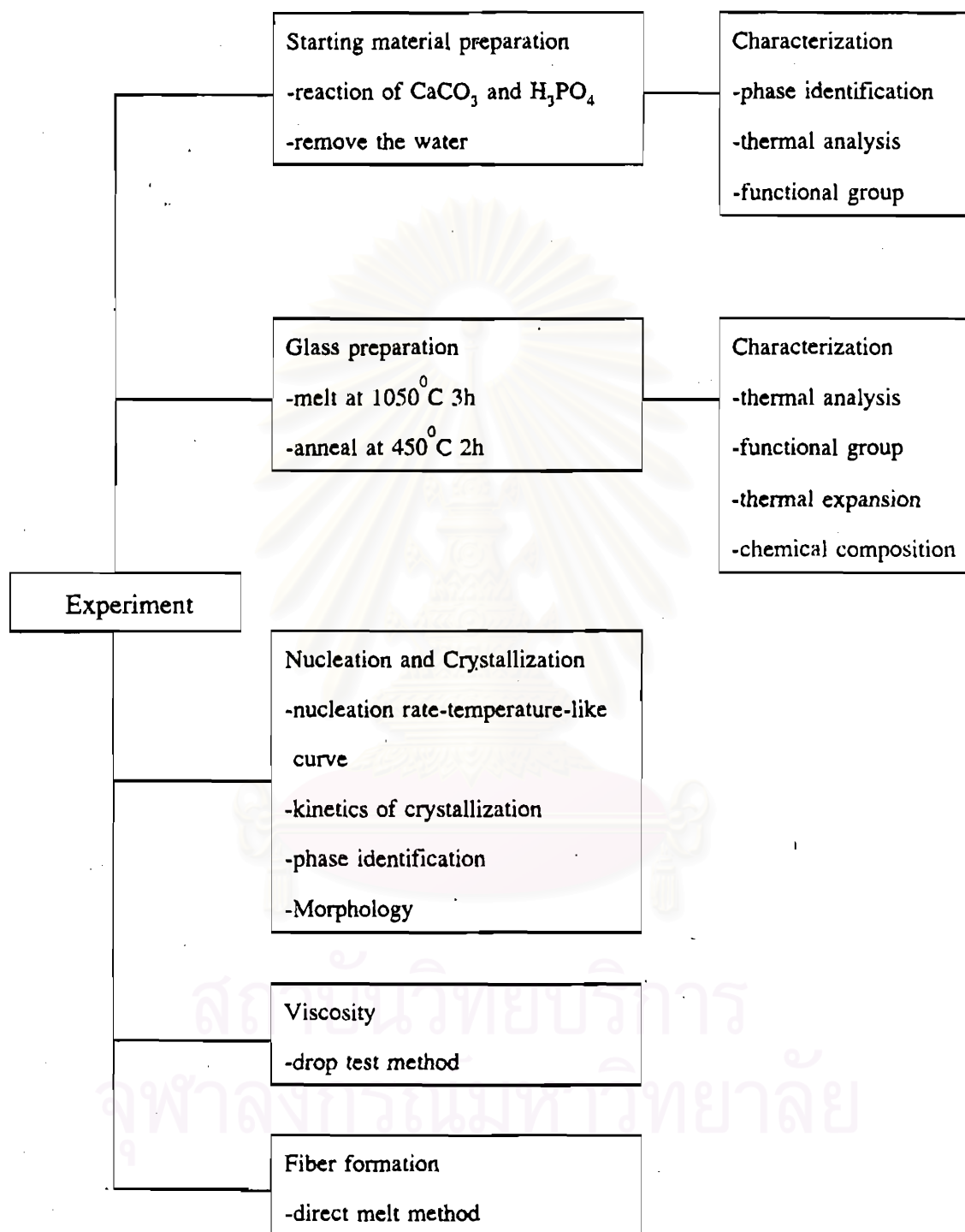


Figure 3-2 Experimental description flow chart

3.2 Experimental procedure

3.2.1 Starting materials preparation

Three compositions of starting materials were chosen from the phase diagram CaO-P₂O₅ system (in Figure 3-1) as illustrated in Table 3-1.

Table 3-1 Starting materials compositions and codes

Composition No.	Code No.	CaO : P ₂ O ₅ (mol%)
1	CP1	50 : 50
2	CP2	51.1 : 48.9
3	CP3	51.9 : 48.1

These starting materials were prepared by reacting calcium carbonate* (CaCO₃) with orthophosphoric acid** (H₃PO₄) in mol% ratio. The mixture was stirred over night to ensure that the evolution of carbon dioxide had stopped. The mixture was dried at 100 °C to evaporate the water. The dried mixture was crushed to fine powder and stored.

* 99.5% Calcium carbonate, AR grade of Carlo Erba

** 85% Phosphoric acid, AR grade of Carlo Erba

3.2.2 Starting materials characterization

The prepared starting materials were characterized as follows:

3.2.2.1 Thermal analysis

The thermal analysis of starting materials was characterized by differential thermal analysis (DTA) and thermal gravimetric analysis (TG). The starting materials were crushed to fine powder and examined the thermal reaction, % weight loss and liquidus temperature by using SETARAM TGDTA 92 thermal analyzer. The sample was run in a Pt crucible with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from 20 ° to $1100\text{ }^{\circ}\text{C}$ in the static air.

3.2.2.2 Phase identification

The phases of the starting materials were characterized by X-ray diffraction (XRD). They were crushed to fine powder and examined crystal phases using Philip diffractometer (PW 1730/10) with copper K_{α} radiation at 30 mA and 40 kV and nickel filter. A time constant of 1 sec and a scanning rate of 2 min^{-1} were used. The XRD patterns were recorded with a chart drive speed of 2 cm/min and the 2θ value were varied from 10° to 50° . The crystal phases at different temperatures were examined to observe the phase change.

3.2.2.3 Functional groups

The functional groups of the starting materials were characterized by Fourier Transform Infrared Spectrophotometer (FT-IR 1760 X Perkin-Elmer). The sample preparation used KBr disc method. The FT-IR spectra were recorded with wave number varied from 4000 to 450 cm^{-1} .

3.2.3 Glass preparation

Before melting, each type of starting materials (CP1, CP2, and CP3) was calcined at 550 °C for 2 h to remove hydrate form. The starting materials were melted in the clay crucible* at 1050 °C for 3 h. During melting there was the partially corrosion between the glass and the clay crucible. CP1 which contained $\text{CaO}:\text{P}_2\text{O}_5 = 50:50$ mol% was chosen to melt in a Pt crucible to prevent the corrosion. Thus the glass samples were classified into 4 types as illustrated in Figure 3-3.

*clay crucible from G.S. Ceramics Co.,Ltd.

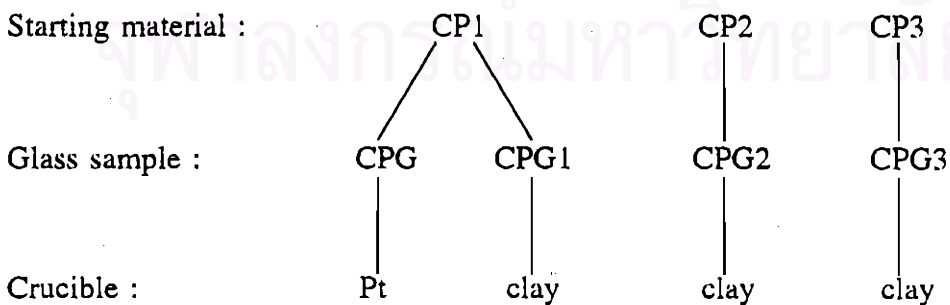


Figure 3-3 Four types of glass samples and codes.

After melting, the glass sample was casted in a graphite mold and annealed to release the stress at 450 °C for 2 h.

3.2.4 Glass characterization

3.2.4.1 Chemical composition

After melting, the mole ratio of CaO : P₂O₅ of glass was determined by wet chemical analysis.

Determination of CaO by precipitate of CaC₂O₄·H₂O:

0.1 g glass sample was dissolved in 3 ml 5 M HCl and heated until the solid has dissolved then diluted to about 100 ml with deionized water. 2 drops of methyl red indicator was added to the sample solution. 2.0 g ammonium oxalate [(NH₄)₂C₂O₄] was dissolved in 50 ml of water then put into the sample solution. The ammonia solution (1:1) was dropped slowly into the sample solution with stirring until the sample solution changed the colour from red to yellow. The sample solution was heated again to complete the reaction and allowed to stand without further heating for at least an hour. The precipitate of CaC₂O₄·H₂O settled. After that CaC₂O₄·H₂O was filtered into a sintered glass filter, washed with diluted [(NH₄)₂C₂O₄] and then one wash with deionized water, followed by two washes with acetone. The precipitate of CaC₂O₄·H₂O was dried at 50 °C and then weighed.

$$\% \text{ CaO} = \frac{0.3836 \times 100 \times \text{wt. of CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}}{\text{sample weight}}$$

Determination of P_2O_5 by molybdovanadate method

0.1 g glass sample was dissolved in 3 ml 5 M HCl and heated until the solid has dissolved then diluted to 1000 ml in a volumetric flask. 3 ml of the samples solution was pipetted and diluted to 25 ml in a volumetric flask. The amount of P_2O_5 was measured with DR/1 A colorimeter., The sample solution was filled in a sample cell and the deionized water was filled in another sample cell for the reagent blank. Using the calibrated dropper 1.0 ml of molybdovanadate reagent was added to each sample cell and allowed 3 min for full colour development. (A yellow colour will develop if phosphate is present). The treated reagent blank was placed into the cell holder and selected the 420 nm colour filter. Then the meter was calibrated with reagent blank. The prepared sample solution was placed into the cell holder closed the light shield and read the mg/L orthophosphate (PO_4) or mg/L phosphorus pentoxide (P_2O_5) multiplying by 0.75

The amount of P_2O_5 of sample was extrapolated from the P_2O_5 standard curve as illustrated in Figure 3-4

(Note : The preparation of P_2O_5 standard was used by adding 2, 4, 6, 8, and 10 ml. of the 50 mg/L phosphate (PO_4) standard solution in 25 ml. volumetric flask and diluted to 25 ml. with deionized water. The concentration would be 3, 6, 9, 12 and 15 mg/ L as P_2O_5 , respectively.)

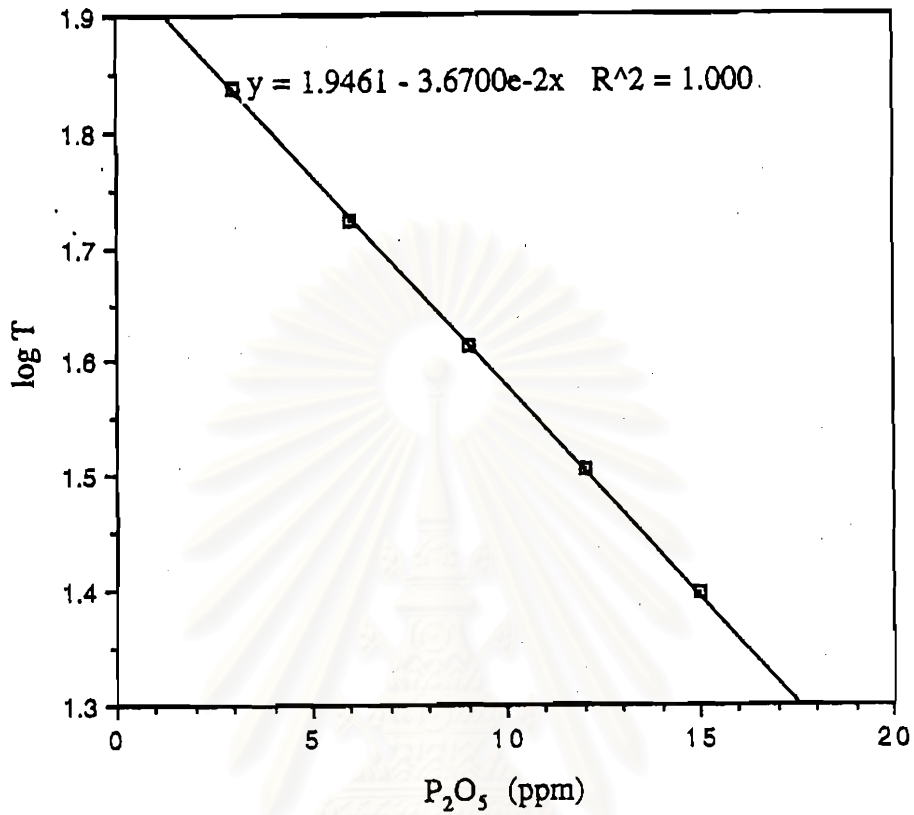


Figure 3-4 P₂O₅ standard curve

The glass samples were determined the composition again by using XRF borate fusion method which were done by Mineral Assays and Service Co., Ltd.

3.2.4.2 Functional groups

The functional groups of the glass samples were characterized by the similar method as described in 3.2.2.3.

3.2.4.3 Thermal expansion coefficient

The thermal expansion coefficients of each CPG, CPG1, CPG2, and CPG3 glass samples were measured by an Adamel Lhomaegy DI-24 dilatometer with the heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. From this experiment the transition temperature and the softening temperature were observed, as illustrated in Figure 3-5.

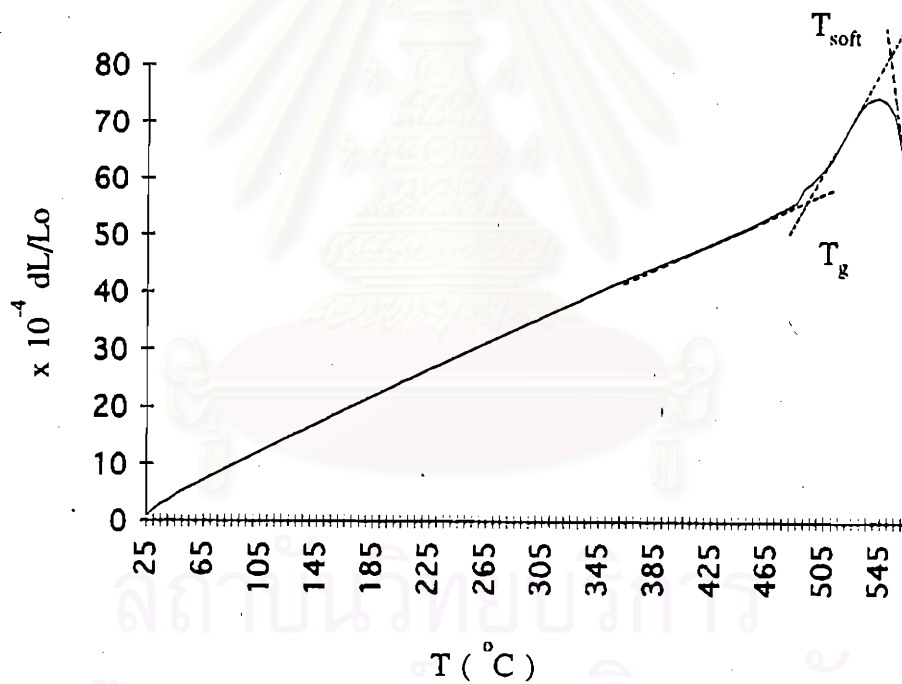


Figure 3-5 Thermal expansion coefficient of glass.

3.2.4.4 Thermal analysis

The glass samples were characterized by the similar method as described in 3.2.2.1. DTA curve showed three main points: transition, crystallization, and melting point as shown in Figure 3-6.

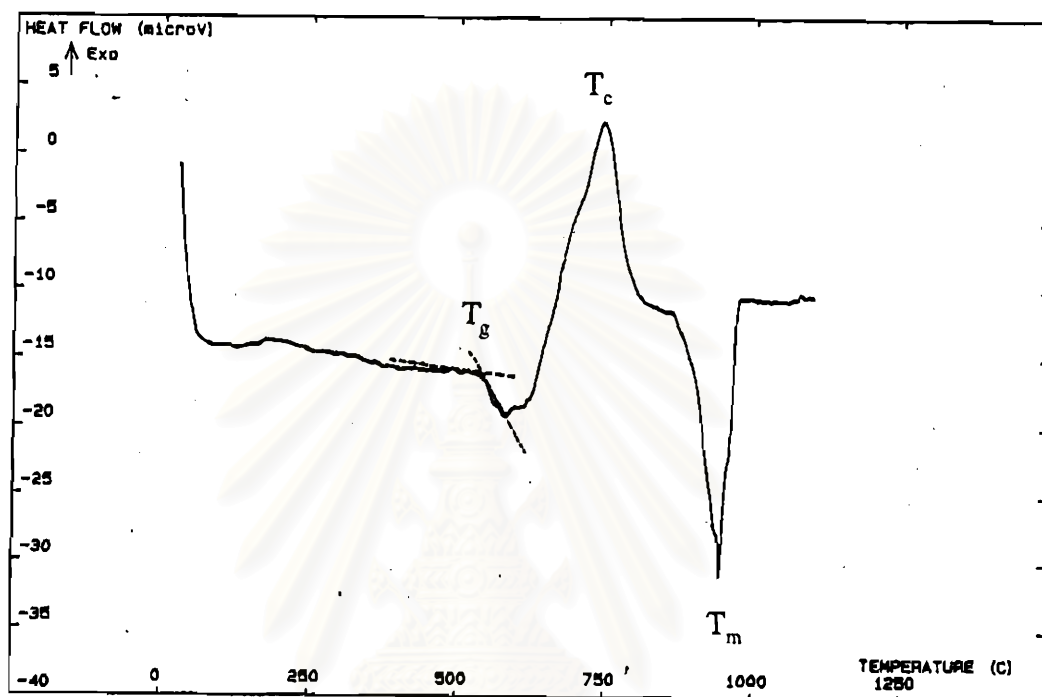


Figure 3-6 DTA curve transformation of glass .

3.2.5 Determination of nucleation and crystallization

Each CPG, CPG1, CPG2, and CPG3 glass samples were prepared by melting and quenching rapidly to the room temperature. The as-quenched glass samples were crushed to obtain powdered samples ($< 45 \mu\text{m}$) and washed with acetone and poured it off by repeating until acetone was clear after last washing. By this method the powdered samples would be of the same size. After that they were stored in a dessicator to prevent moisture attack before DTA measurements.

3.2.5.1 Determination of nucleation rate-temperature

like curve

The DTA measurements were performed using about 50 mg of each CPG, CPG1, CPG2, CPG3 glass samples in a Pt crucible in a static air. Firstly, the glass sample was heated at $50\text{ }^{\circ}\text{C}/\text{min}$ until it reached the selected nucleation temperature. Then the glass sample was nucleated isothermally in the DTA apparatus (Netzsch STA409) at the selected temperature for 2 h. (CPG glass samples were nucleated at the temperature between $450\text{ }^{\circ}\text{C}$ - $500\text{ }^{\circ}\text{C}$, between $560\text{ }^{\circ}\text{C}$ - $620\text{ }^{\circ}\text{C}$ for CPG1, between $540\text{ }^{\circ}\text{C}$ - $580\text{ }^{\circ}\text{C}$ for CPG2, between $530\text{ }^{\circ}\text{C}$ - $600\text{ }^{\circ}\text{C}$ for CPG3). Finally, the glass sample was heated continuously without removal from the DTA apparatus, at $10\text{ }^{\circ}\text{C}/\text{min}$ until the crystallization peak was completed about $800\text{ }^{\circ}\text{C}$. The crystallization peak temperature (T_p) and the nucleation temperature (T_n) were recorded. The graph of $1000/T_p$ versus T_n was plotted to determine the maximum nucleation temperature.

3.2.5.2 Determination of kinetics of crystallization by nonisothermal method.

The CPG, CPG1, CPG2, and CPG3 glass samples were heated at different heating rates (α), which were 5, 8, 10, 12, and $15\text{ }^{\circ}\text{C}/\text{min}$ from $20\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ in the DTA apparatus (SETERAM TGDTA92). The crystallization peak temperatures (T_p) at different heating rates were recorded and the width of the crystallization peak at half maximum was measured; each activation energy of crystallization of glass sample was determined by a

plot of $\ln(T_p^2/\alpha)$ versus $1000/T_p$, the activation energy of crystallization was taken as the slope of the line. Avrami parameter (n) which was related to the directionality of crystal growth was determined from the shape of the DTA crystallization exothermic peak using the equation

$$n = (2.5 / \Delta T) (RT_p^2 / E)$$

where ΔT - the width of the crystallization peak at half maximum

R - gas constant

T_p - the crystallization peak temperature

and E - the activation energy of crystallization.

3.2.5.3 Morphology

The nuclei which occurred on the glass surface was examined by using a Scanning Electron Microscope (SEM), Joel JSM-5410LV type. The pieces of CPG, CPG1, CPG2 and CPG3 glass samples were polished with alumina powders (BUEHLER[®] micropolish) of various fineness: 1.0, 0.3, and 0.05 μm in diameter, respectively. Then the pieces of glass were cleaned with acetone in the ultrasonic bath. After that the pieces of glass were heated isothermally in the furnace for 10 min, 30 min, 2 h, 5 h, 10 h, and 24 h at the maximum nucleation temperature (T_n). Finally, the pieces of glass were etched in 0.25 % H_3PO_4 solution for 15 sec at room temperature before coating with gold.

3.2.5.4 Phase identification

The CPG , CPG1 , CPG2 and CPG3 glass samples were heated at the temperature between 550° - 950 °C for 2 h in the furnace. Then the glass samples were crushed to fine powder and the crystal phases were examined by X-ray diffraction (XRD)

3.2.6 Viscosity

The viscosity of CPG, CPG1, CPG2, and CPG3 glass samples were examined by using the drop test method. A fast heating high temperature furnace (Haraeus type K1700/1) with an accurate temperature control and an orifice (about 1 cm) in the bottom was used each to CPG, CPG1, CPG2, and CPG3 glass samples would be crushed as cullet sample (15 - 20 g, grain size 2 - 5 mm) was put into a small clay crucible which a 3 mm orifice in the bottom. The crucible was placed onto a refractory ring support in the furnace and heated to the desired temperature level (CPG at about 1140 °C, CPG1 at 1080°C, CPG2 at 1060°C, and CPG3 at 1080 °C). While the first drop was falling, the time was started to record. The drops after time were weighed. Finally, the cumulative drop weight was plotted with the time. Figure 3-8 illustrated the drop test method. A steady state was reached with a constant slope $\beta = \partial m / \partial t$. The slope β was inversely proportional to the viscosity:

$$\eta = C / \beta$$

where η = viscosity, C = calibration constant per 100 sec,
and β = slope of the graph

By the same method, JM-753 glass was used to determine the calibration constant by using VFT-equation to calculate the viscosity and the slope attained from the graph. (A, B, and T_0 values of JM-753 glass can be seen in Appendix A)

At 1215 °C the viscosity of JM-753 glass was 250.03 Pa.s and the slope of the line was 55.998. Thus calibration constant per 100 sec (C) was 140.02.

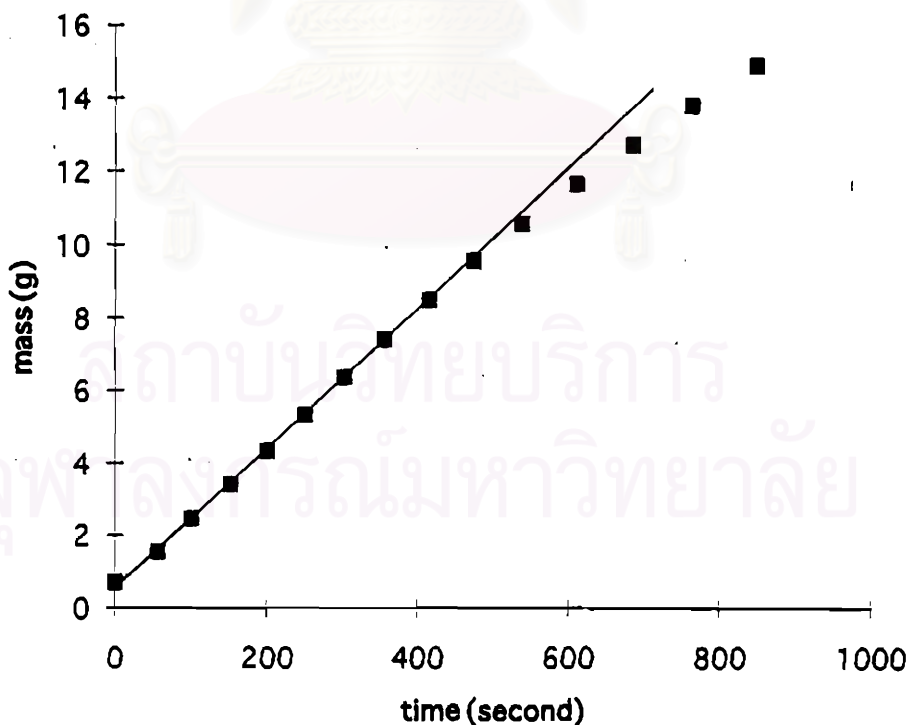


Figure 3-7 Plot of cumulative mass vs time of JM-753 glass.

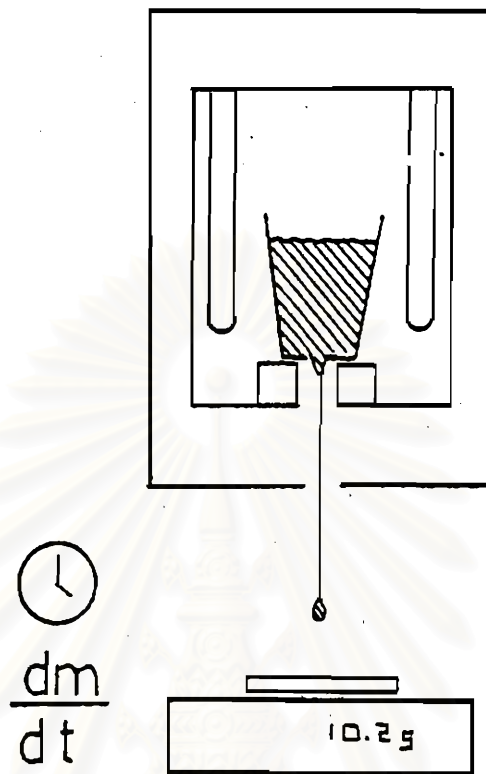


Figure 3-8 Illustration of drop test method.

3.2.5 Forming of glass fiber

Each CPG, CPG1, CPG2, and CPG3 glass samples was melted in a crucible which had a 3 mm. orifice in the bottom. Heated the glass sample about 1100 °C, depending on the type of glass. The molten glass failed

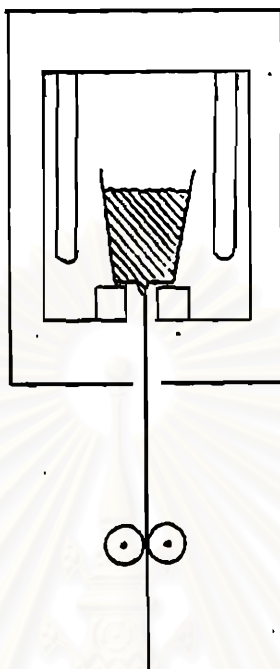


Figure 3-9 The formation of glass fiber with the drawing machine.

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