

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Vinyl Chloride Monomer (VCM)

Vinyl chloride monomer (VCM) was a commercial product of the Thai Plastic and Chemicals Public Company Limited (TPC).

This monomer had a purity content of 99.5% by weight, iron content of 1.0 ppm by weight, chlorinated hydrocarbon content of 200 ppm by weight and inhibitor content of 10.0 ppm. by weight.

The general properties of VCM at ambient temperature and pressure are colorless gas with faintly sweet odor. VCM is mildly toxic which has flammable limit of 3.6% to 26.4% by volume in air. It can form explosive mixtures with air at normal ambient temperature.⁽⁸⁾

3.1.2 Organic Peroxide

Industrial grade organic peroxide was employed as an initiator. This material has a half-life of 10 hours at 62°C.

3.1.3 Chain Transfer Agent

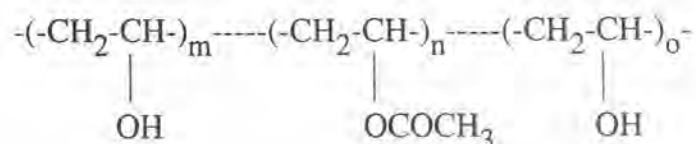
A mercapto-containing organic compound was used as a chain transfer agent.

3.1.4 Demineralized Water

The demineralized water used had a quoted pH of 6-7, conductivity of 2.0 microseimen, SiO₂ content of 1.0 ppm and iron content of 0.05 ppm.

3.1.5 Suspending Agent

Two suspending agent groups were used in this work. They are partially hydrolyzed poly(vinyl acetate) (PVA) and substituted cellulose. The partially hydrolyzed PVA was a commercial product with the following structure.



$$\text{where mole\% of degree of hydrolysis} = 100(m+o)/(m+n+o) \text{ -----(13)}$$

For convenience, these suspending agent are designated as PVA-1 and PVA-2. The PVA-1 had a degree of hydrolysis of 69-75 mole%. The viscosity of 4 wt% solution at 20°C was given from the supplier as 4-6 cps. The PVA-2 had a degree of hydrolysis of 78-82 mole%. The viscosity of 4 wt% solution at 20°C was given from the supplier as 29-38 cps. The substituted cellulose had a methoxy content of 28-30 wt% and hydroxypropoxy content of 7-12 wt%. The viscosity of 2% solution at 20°C was given from the supplier as 40-60 cps.

3.2 Equipment and Apparatus

3.2.1 Four litre stainless steel reactor with a jacket and automatic controlled temperature system (Parr 4555)

3.2.2 Dosing pump (Gamma 4/w 2001S)

3.2.3 Labo type fluidized bed dryer was used for drying PVC.

3.2.4 Thermostatic water bath (Lauda Dlk30 & CD30) and viscometer, Ubbelohde type which having a inner diameter capillary of 0.53 mm.

3.2.5 Sieve and mechanical sieving device (Retsch)

3.2.6 Bulk density apparatus (made by TPC under the reference test method ISO 60)

3.2.7 Centrifuge (IEC HN-SII)

3.2.8 Two roll mill (Lab Tech LRM i50)

3.2.9 Hydraulic pressing machine (Lab Tech LP-50)

3.2.10 Oil bath (Heto DBT623)

3.2.11 Brabender Plastic-corder (PL2000)

3.2.12 Izod impact strength tester (Toyoseiki)

3.2.13 Heat deflection temperature tester (Rosand ASP-6)

3.2.14 Melt flow index tester (Toyoseiki T-1001)

3.2.15 Scanning electron microscope (JSM-5410LV)

3.3 Procedure

3.3.1 General Procedure for the Preparation of PVC Resin.

PVC resin with K-value of 50 ± 1 was prepared by VCM suspension polymerization. Demineralized water, suspending agent and initiator were charged into four litre stainless steel autoclave and stirred mechanically for

homogeneity at 50 rpm. Then the autoclave was evacuated to eliminate oxygen. After that the VCM was charged into autoclave with controlled stirring at 670 rpm and the mixture was heated to the reaction temperature. Due to the nature of suspension polymerization, a heat occurred in the reaction; therefore, the cooling water was used by passing through the jacket of the autoclave to remove this heat. The reaction time was controlled by adjusting the amount of initiator. In this investigation, the reaction time was 5 hours \pm 15 minutes. The polymerization was terminated by venting off the remaining VCM in autoclave. Finally, the PVC resins were filtered and dried in the fluidized bed dryer.

3.3.1.1 Polymerization of Low Molecular Weight PVC Resin without Chain Transfer Agent.

This step was a polymerization of PVC resin with K-value of 50 ± 1 at high temperature without the addition of chain transfer agent. The temperatures of polymerization employed were 69, 73, 75, 77, 81, and 82°C to find the most suitable temperature for the preparation of PVC resin. The flow-chart of procedure for the preparation of low molecular weight PVC resin by polymerization at high temperature is shown in Figure 3.1.

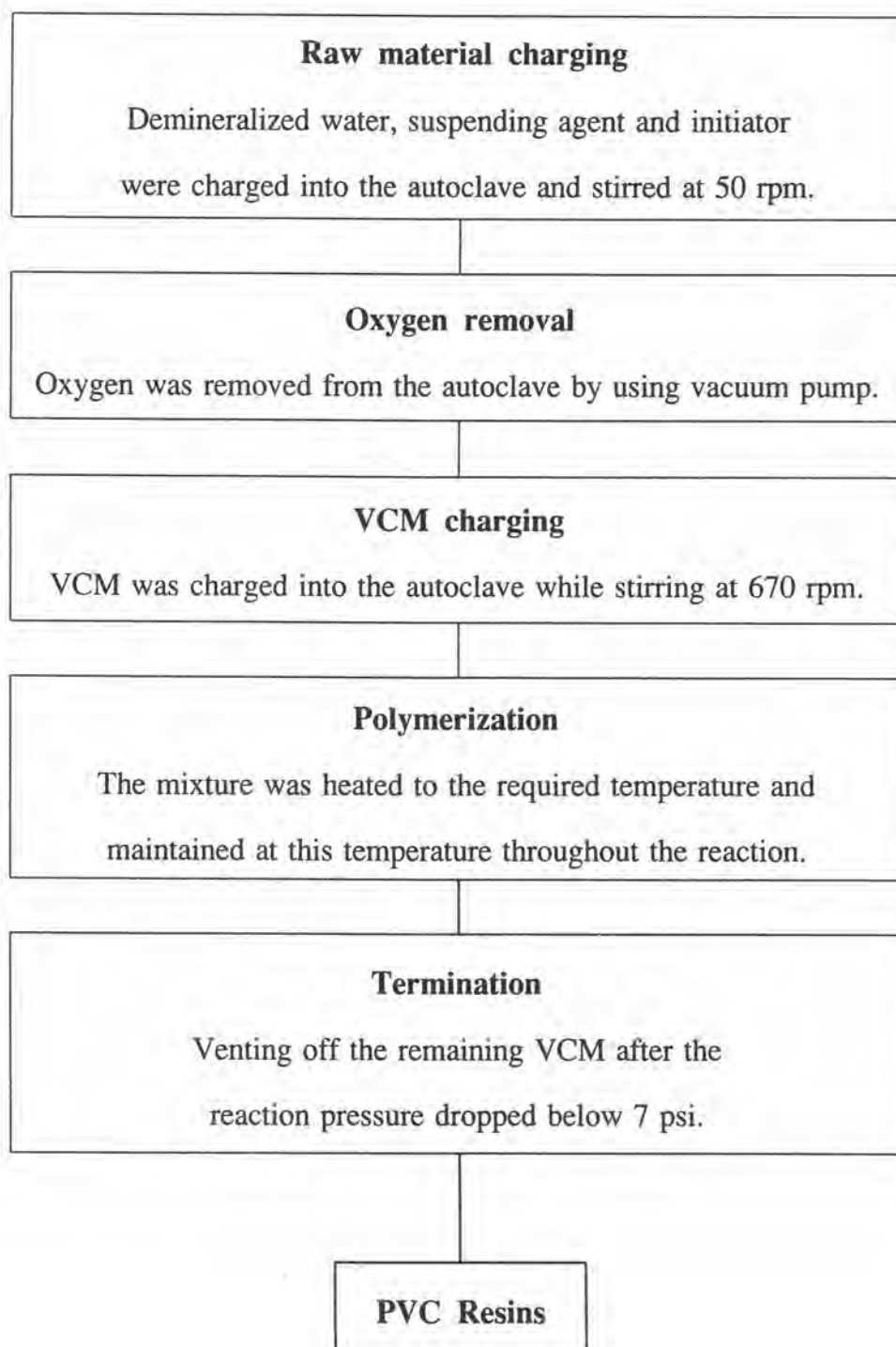


Figure 3.1 Procedure for the polymerization of low molecular weight PVC resin without chain transfer agent.

3.3.1.2 Polymerization of Low Molecular Weight PVC Resin in the Presence of Chain Transfer Agent.

The polymerization temperature and amounts of chain transfer agent employed are shown in Table 3.1

Table 3.1 Amount of chain transfer agent used for various K-value of PVC

Polymerization temperature($^{\circ}$ C)	Amount of chain transfer agent (phm)
77	0, 0.02, 0.04, 0.08
73	0, 0.04, 0.08, 0.12
69	0, 0.04, 0.08, 0.12

The flow-chart of this procedure as shown in Figure 3.2.

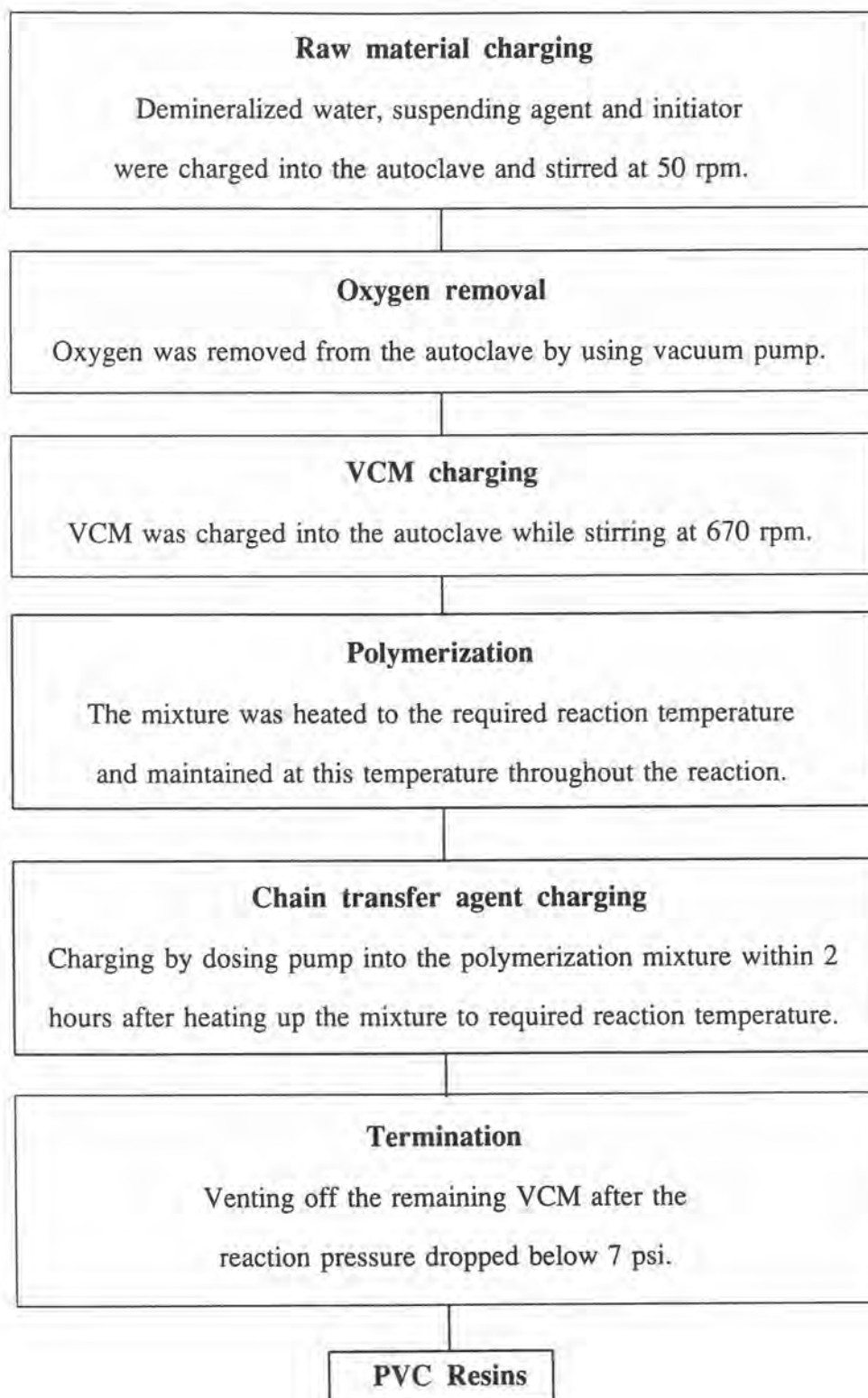


Figure 3.2 Procedure for the polymerization of low molecular weight PVC resin in the presence of chain transfer agent.

3.3.2 Polymerization Parameters

3.3.2.1 Water : VCM ratio

The water : VCM ratio was fixed at 1.5.

3.3.2.2 Total Volume of The Polymerization Mixture.

Total volume of the polymerization mixture at the polymerization temperature was about 75% of the autoclave volume. Therefore, density was considered the most important polymerization parameter at different temperatures. A table of density values at various temperatures is given in Appendix. The amount of VCM and water was calculated as follows:

$$\text{Charge volume} = \frac{(\text{water:VCM})(m_{\text{VCM}})}{\rho_{\text{w}}} + \frac{(m_{\text{VCM}})}{\rho_{\text{VCM}}} \quad \text{-----(14)}$$

Where

water : VCM = water/VCM ratio

m_{VCM} = mass of VCM

ρ_{w} = density of water at the polymerization temperature

ρ_{VCM} = is a density of VCM at the polymerization temperature

3.3.2.3 Chain Transfer Agent Charging Time

In this investigation, chain transfer agent charging time was 2 hours \pm 15 minutes.

3.3.2.4 Reaction Time

Reaction time was 5 hours \pm 15 minutes.

3.3.3 Material Testing

3.3.3.1 Properties of Low Molecular Weight PVC Resin

(a) Mean Particle Size

Mean particle size can be calculated according to ASTM D-1921-89.

(b) Calculation of Distribution Coefficient of Particle Size

The distribution coefficient of particle size was obtained from the plot between sieve size and cumulative weight percent of PVC retained on the sieve. Thus the distribution coefficient of particle size can be calculated by using this curve and the equation as shown below:

$$\text{Size distribution coefficient} = (S_{84} - S_{16}) / (2 \times S_{50}) \quad \text{-----(15)}$$

where

S_{84} = cumulative weight percent on sieve size of 84 micrometer

S_{50} = cumulative weight percent on sieve size of 50 micrometer

S_{16} = cumulative weight percent on sieve size of 16 micrometer

(c) Bulk Density

Determined by using standard method of ISO 60-77.

(d) Cold Plasticizer Absorption (CPA)

This test method was developed by TPC as follows:

- (1) 3 grams of PVC resin was weighted and poured onto a sinter glass.

(2) 3.5 grams of dioctyl phthalate (DOP) was added and allowed for a period of 1 hour to absorb DOP into the porous of PVC resin.

(3) Then the resin was centrifuged at 3,000 rpm for a period of 1 hour to remove the excess DOP.

(4) Weigh the resin to find the absorbed DOP and calculate the percentage of plasticizer (DOP) using the equation

$$\text{CPA} = \frac{\text{weight of plasticizer absorbed} \times 100}{\text{weight of PVC resin}} \text{ -----(16)}$$

(e) Fish eyes

This test method was developed by TPC as follows:

(1) Preparation of Dry blend

PVC resin	100 parts
Plasticizer (DOP)	60 parts
Stabilizer (Ba/Cd/Zn soaps)	3.3 parts
Pigment (carbon black)	0.33 parts

(2) Mixed a dry blend in two roll mill at 145°C for 5 minutes. Then, a milled sheet of 0.35-0.40 mm. thickness was selected.

(3) The milled sheet was used to determine the amount of fish eyes (ungel particle) in the area of 15 cm x 21 cm.

(f) K-value of vinyl chloride polymers

The K-values of PVC were determined in a solution using DIN 53726. PVC (0.5 g) was dissolved in cyclohexanone (100 ml) at 25°C to obtain a solution of 0.5% w/v concentration.

3.3.3.2 Properties of Low Molecular Weight PVC Dry Blend

The formulation of low molecular weight PVC dry blend for rigid application was shown as follows:

PVC	100	part
Processing aid (Acrylic resin)	1.0	part
Internal lubricant (Glycerol monostearate)	1.0	part
External lubricant (High density oxidized polyethylene)	0.3	part
Stabilizer (Methyl tin mercaptide)	1.5	part

(a) Static Heat Stability

The PVC dry blend were mixed in a two roll mill at 160°C for 7 minutes. The milled sheets of 1.0 mm thickness were cut into a small pieces. Then small pieces were placed in a test tube. The test tube was dipped in a oil bath at 180°C. The samples were taken away gradually every 5 or 10 minutes until the milled sheets changes to the black color.

(b) Dynamic Heat Stability

Dynamic heat test, the sample was not only thermally stressed but also subjected to shearing forces.⁽⁹⁾ Two methods employed were

- Continuous rolling method

PVC dry blends were fused on the two roll mill whose diameter of roller gap was 1 mm at 180°C. The samples were stressed continuously on the mill. The samples were cut from the center of sheet every 5 minutes until the sample sheet changed to the black color.

- Kneading chamber of a plastograph

The measurements were performed on a Brabender Plasti-corder . The mixing head (30 grams in weight) was used. The mixer was preheated at 180°C. A weighed quantity of PVC dryblend was introduced into the chamber (head cavity) with the rotor running at 40 rpm. The load used in this study was 5 kg/cm². The time was determined from the start of mixing to the rise of torque indicating the decomposition point.

(c) Fusion Torque

The measurements were performed on a Brabender Plasti-corder. The mixing head (50 grams in weight) was used. The mixer was preheated at 100°C. A weighed quantity of PVC dry blend was introduced into the chamber with the rotor running at 30 rpm. The load used in this study was 5 kg/cm². The fusion torque was determined at maximum torque.

(d) Heat Deflection Temperature (HDT)

Performed by using standard test method of ASTM D-648. The sample size was 3 mm x 12.7 mm x 130 mm.

(e) Izod Impact Strength

Determined according to standard test method of ASTM D-256 (method A).

(f) Melt Flow Index

Measured at 200°C with 10 kgs load according to ASTM D-1238.