CHAPTER III

EXPERIMENTAL

3.1 Materials

Five materials were used for VCM suspension polymerization as the following.

3.1.1 Demineralized Water

Some important properties of demineralized water which have to be controlled are:

Iron content	(ppm. wt/vol)	0.05 max.
SiO_2	(ppm. wt/vol)	1.0 max.
Conductivity	(microseimen)	2.0 max.

3.1.2 Vinyl Chloride Monomer (VCM)

CH_2=CHCl

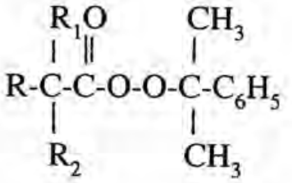
Some important properties of VCM which have to be controlled are:

VCM purity	(%)	99.5 min.
Iron content	(ppm)	1.0 max.
Inhibitor	(ppm)	10.0 max.
Chlorinated hydrocarbon	(ppm)	200.0 max.

3.1.3 Initiator

An organic peroxide having a half-life of 10 hours at 36 and 43°C was used.

1. Initiator with a half-life of 10 hours at 36°C



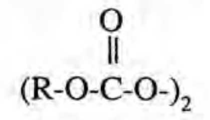
$$R-\underset{R_2}{\overset{R_1}{C}}-\overset{O}{\overset{\|}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5$$

where R_1 and R_2 = CH_3 or C_2H_5

$R = C_4H_9$, C_5H_{11} or C_6H_{13}

$R+R_1+R_2= 8C$

2. Initiator with a half-life of 10 hours at 43°C

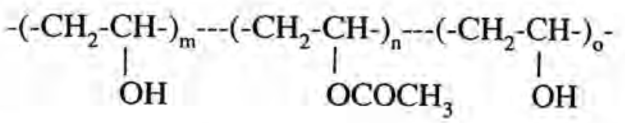


$$(R-O-\overset{O}{\overset{\|}{C}}-O-)_2$$

where R = Alkyl group

3.1.4 Suspending Agent

Partially hydrolyzed poly(vinyl alcohol) is used for stabilizing the monomer droplets. There were two grades, the first grade with a degree of hydrolysis of 69-75 mole% and viscosity of 4% aqueous solution at 20°C was 4-6 cps.; and the second one with a degree of hydrolysis of 78-82 mole% and viscosity was 29-38 cps. The possible structure is:



$$-(-CH_2-\underset{\substack{|\\ OH}}{CH}-)_m---(-CH_2-\underset{\substack{|\\ OCOCH_3}}{CH}-)_n---(-CH_2-\underset{\substack{|\\ OH}}{CH}-)_o-$$

.... (11)

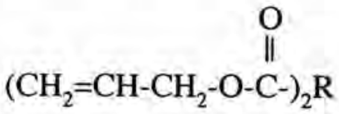
while

$100(m+o)/(m+n+o)$ = mole% of degree of hydrolysis .... (12)

The ratio by weight of the low and high degrees of hydrolysis of the suspending agent used in this work is 70 to 30.

3.1.5 Multiunsaturated Comonomer

In this work, diallyl ester (Asian Scientific) was used. Its functional structure is as follows:



$$(CH_2=CH-CH_2-O-\overset{\substack{O\\ \|}}{C}-)_2R$$

.... (13)

where R = alkyl group

3.2 Equipment and Apparatus

3.2.1. Twenty litre stainless steel autoclave with a jacket (Parr 4843) used for VCM suspension polymerization.

3.2.2. Forced air flow oven (WFO-600-ND) used for drying PVC cake.

3.2.3. An Ubbelohde type viscometer with 0.52 ± 0.04 mm. inner diameter capillary tube and a thermostatic water bath (LAUDA DLK 30 & CD30) used for the determination of degree of polymerization.

3.2.4. Sieve and mechanical sieving device with time switch (Retch) used for particle size determination (sieve analysis).

3.2.5. Bulk density apparatus (made by TPC under the specification of the reference test method)

3.2.6. Centrifuger (JEC HN-SII) used for removing excess plasticizer from PVC resin in order to determine the cold plasticizer absorption of PVC resin.

3.2.7 Laboratory two roll mill (LRM 150) used for preparing milled sheets for property tests.

3.2.8. Infrared dryer (Mettler LP-16M) used for determining moisture content in dried PVC.

3.2.9. Hydraulic pressing machine (LP-50) used for preparing pressed sheet from milled sheet in order to obtain the specified thickness.

3.2.10. Hardness tester (Zwick 7206).

3.2.11. Tension tester (Toyoseiki Strograph RS 500).

3.2.12. Brittleness temperature tester (Toyoseiki Seisanu 121202).

3.2.13. Ultramegohmmeter (TOA SM-10E) used for volume resistivity determination.

3.2.14. Parallel plate plastometer (Toyoseiki TDM-1030) used for determining heat deformation of the sample sheet.

3.3 Procedure

There were two parts of the experiment. The first part was to synthesize UHMW PVC resins by the addition of multiunsaturated comonomer. The second part was to study the effect of multiunsaturated comonomer on UHMW PVC properties.

3.3.1 Synthesis of UHMW PVC Resin by Addition of Multiunsaturated Comonomer.

VCM suspension polymerization was carried out in a twenty litre stainless steel autoclave with a jacket. All raw materials were mixed in the autoclave except VCM then the autoclave was sealed and evacuated. After that VCM was charged and the mixture was heated up to the polymerization temperature using hot water in the autoclave jacket as a heat transfer medium. Once it reached the set temperature, polymerization started and heat was evolved. This heat was removed by chilling water in the autoclave jacket. The autoclave pressure was steady until no VCM phase was remaining then the pressure began to fall. When the set pressure reached, the polymerization was terminated by venting off the excess VCM. After that the autoclave was unsealed, PVC slurry was filtered and then dried until the moisture content was 0.3% or lower.

In this work, the degree of polymerization ($\overline{DP}$) value was used as an index to classify the molecular weight of PVC. This value was obtained by determining the relative viscosity (JIS K 6721) between dilute PVC solution and pure solvent (Nitrobenzene). The target of $\overline{DP}$ value was 2500 ± 50.

There were six polymerization temperatures understudy which were 40, 43, 46, 49, 52 and 58°C. At each polymerization temperature, there were influencial conditions needed to be controlled. These were: reaction time, total volume of the mixture in the autoclave, and the ratio of water to VCM.

3.3.1.1 Important Reaction Parameters for PVC Polymerization

1. Reaction Time

In this work, the reaction time was the time started from heating up finished to 0.5 kg/cm^2 pressure dropped from the reaction pressure. The reaction time of all polymerizations was controlled at around 360 ± 20 minutes by adjusting the amount of initiator used. A higher amount of initiator offered a shorter reaction time.

2. Total Volume of The Mixture in The Autoclave

Since the density of VCM changed with temperature, thus the amount of VCM for different polymerization temperatures must be different. The VCM amount was decreased at higher polymerization temperatures in order to keep a total volume of the mixture at around 75% of the autoclave volume.

3. Ratio of Water:VCM

In this work, the water:VCM ratio was fixed at 2.3 and the agitator speed was fixed at 500 rpm.

3.3.1.2 Testing Procedure

The experiment was started by synthesizing the reference UHMW PVC resin without the addition of multiunsaturated comonomer at the polymerization temperature of 40°C as the formulation shown in Table A-1 in Appendix A. Then the $\overline{DP}$ of PVC resin was determined. After $\overline{DP}$ was found to be at around 2500 ± 50, the polymerization was repeated in order to confirm the repeatability of experimental results. All wet PVC resins of the repeated batch were dried and %conversion could be calculated from the total weight of dried PVC.

In order to keep $\overline{DP}$ at around 2500 ± 50 for higher polymerization temperatures, a multiunsaturated comonomer was added. The amount of comonomer was different at different polymerization temperatures. Thus the effects of comonomer amount and polymerization temperature on $\overline{DP}$ of UHMW PVC resin were studied. In this work, UHMW PVC resins with $\overline{DP}$ of 2500 ± 50 were synthesized at five different polymerization temperatures from which the $\overline{DP}$ of PVC resin was controlled by using a multiunsaturated comonomer. At each polymerization temperature, a synthesis of PVC resin without multiunsaturated comonomer was carried out first. Then the $\overline{DP}$ of PVC resin so obtained was determined. After that, other UHMW PVC resins were synthesized by addition of a multiunsaturated comonomer. The amount of comonomer was varied from 0 to 0.1, 0 to 0.2, 0 to 0.25, 0 to 0.3 and 0 to 0.31 part by weight of VCM amount at 43, 46, 49, 52 and 58°C, respectively. All the formulations were shown in Tables A-2 to A-6 in Appendix A. The next experiment, the comonomer amount was estimated from the plot of comonomer amount and $\overline{DP}$ from which the target $\overline{DP}$ can be estimated as close as possible. When the $\overline{DP}$ was in the specification, the polymerization was confirmed and $\overline{DP}$ of the PVC resin so obtained was determined. After all the results were in an acceptable range then all the wet PVC resins of the repeated batches were dried and %conversion could be calculated from the total weight of dry PVC. Moisture content of the PVC powder was checked and controlled to around 0.3% or lower.

Very importantly, the initiator amount could be adjusted simultaneously to control the reaction time since it did not impose any effect on $\overline{DP}$ of PVC.

3.3.2 Effect of Multiunsaturated Comonomer on Properties of UHMW PVC

From 3.3.1, there were 6 samples of UHMW PVC resins with the $\overline{DP}$ of 2500 ± 50. These were the reference UHMW PVC resin, and UHMW PVC resins synthesized at 43, 46, 49, 52 and 58°C. The properties of UHMW PVC resin and of UHMW PVC dry blend were studied.

3.3.2.1 Properties of UHMW PVC Resins

3.3.2.1.1 Mean Particle Size

The mean particle size of PVC particle was determined by sieve analysis (ASTM D 1921-89) using 5% ethylene glycol in methanol as antistatic agent. The test method used employs a series of sieves with various opening sizes. The PVC powder with antistatic agent is poured from the top and allows to pass through a series of sieves and is collected at the bottom. The quantity of PVC retained on each sieve is determined by weighing the sieves before and after the test. A shaker is employed to facilitate the separation of various sized particles.

Size distribution coefficient can be obtained from this determination. Relation between sieve size and cumulative weight percent of PVC retained on the sieve was plotted. From the plot, the particle size distribution coefficient was calculated by using the equation below.

$$\text{Size distribution coefficient} = (S_{84}-S_{16})/(2 \times S_{50}) \qquad \text{..........} (14)$$

where S_{84} = cumulative weight percent on sieve of 84 micrometers

S_{50} = cumulative weight percent on sieve of 50 micrometers

S_{16} = cumulative weight percent on sieve of 16 micrometers

3.3.2.1.2 Bulk Density

Bulk density is defined as the weight per unit volume of the resin powder including voids inherent in the PVC as tested. This value is important for determining the weight of polymer that can be accommodated in a given storage vessel. In this work, the reference test method is ISO 60-77.

3.3.2.1.3 Cold Plasticizer Absorption (CPA)

Most of the UHMW PVC resins were used for flexible applications to which resin interaction with plasticizer was important. CPA is the value indicating the level of plasticizer that PVC resin can absorb. The test method used was developed by TPC as follows:

The PVC powder (3.00 g.) was weighed in a sinter glass por. no. 2, then 3.50 g. of plasticizer (dioctyl phthalate) was added. The plasticizer was allowed to fill the pores for 1 hour and the surplus was removed by centrifuging further for 1 hour at 3000 rpm. The plasticizer that is not absorbed by the PVC resins is removed by the centrifugation through the orifice of the sinter glass. After centrifuging, the sinter glass is weighed and the percentage plasticizer absorption is calculated from the difference in the weight of the resin-plasticizer mix(2) as follows:

$$\text{CPA (\%)} = \frac{(\text{weight of plasticizer absorbed} \times 100)}{\text{weight of PVC resin}} \qquad \text{..........} \ (15)$$

3.3.2.1.4 Fisheye

Fisheyes are imperfections in transparent film or sheet which are the results of ungelled PVC particles. The test method used was developed by TPC as follows:

First, the dry blend was prepared by using the formulation below.

UHMW PVC resin	100
Plasticizer (Dioctyl phthalate)	60
Stabilizer (Ba/Cd/Zn soaps)	3.3
Pigment (Carbon black)	0.33

All ingredients were mixed in order to obtain the PVC dry blend. Milled sheet with 0.4 mm. thickness was prepared from this dry blend by milling in a two roll mill at 155°C for 5 minutes. The ungelled particles were counted from milled sheets using the back-light viewing box. The unit of fish eye amount was points per 300 cm^2.

3.3.2.1.5 Moisture Content

This property was checked in order to assure that its content was not higher than 0.3 %, since high moisture content in PVC may be the cause of air bubbles in the finished PVC products which may affect heat stability. The high moisture content offers a better heat stability. The TPC test method was used. An amount of 5-10 g. of PVC powder was weighed in an aluminium pan which was heated later by an IR radiator at 105°C (using an IR dryer) until the sample weight was constant at least for 30 seconds. Moisture content was calculated as follows :

$$\text{Moisture content (\%)} = \frac{[\,A-C\,]}{[\,A-B\,]} \times 100 \qquad \text{.......... (16)}$$

where A = Weight of the pan and PVC powder

B = Weight of the empty pan

C = Weight of the pan and PVC powder after drying

3.3.2.2 Properties of UHMW PVC Dry Blend

The formulation used for preparing UHMW PVC dry blend was the formulation for cable application as follows:

UHMW PVC resin	100
Plasticizer (Dioctyl phthalate)	60
Stabilizer (Tribasic lead sulfate)	3
Internal lubricant (Calcium stearate)	0.1
External lubricant (Polyethylene wax)	0.4

The ingredients were mixed for preparing milled sheets with 1 mm. thickness by a two roll mill at 165°C for 7 minutes. The milled sheets were pressed to obtain the specified thickness as mentioned in the reference test method of each property. Compression pressure used was 150 kg/cm^2 at 150°C for 5 minutes.

Some properties for a cable application were determined. They were hardness, tensile properties, brittleness temperature, volume resistivity, heat deformation, and dynamic heat stability.

3.3.2.2.1 Hardness referring to ASTM D 2240

The durometer hardness test is mostly used for measuring the relative hardness of soft materials. The test method is based on the penetration of a specified indentor force into the material under specified condition.(8)

3.3.2.2.2 Tensile Strength referring to JIS K 6723

Maximum stress is the force which the material has to withstand before the material's failure.(9)

3.3.2.2.3 Elongation referring to JIS K 6723

This value indicates the extent of PVC sample being stretched before the sample breakage.

3.3.2.2.4 Brittleness Temperature referring to JIS K 6723

At low temperatures, all plastics tend to become rigid and brittle, because the mobility of polymer chains is greatly reduced.(8) Brittleness temperature is defined as the lowest temperature at which 100% of the specimens are not broken on impact under the test condition.

3.3.2.2.5 Volume Resistivity referring to JIS K 6723

The volume resistance is defined as the ratio of the direct voltage applied to two electrodes that are in contact with a specimen, to that portion of the current, between them that is distributed through the volume of the specimen. Volume resistivity of material is the electrical resistance between the opposite faces of a unit cube for a given material and at a given temperature.(8)

$$\text{Volume resistivity (VR)} = A.R_v/t \qquad \text{...........} (17)$$

where A = area

t = thickness of specimen

R_v = volume resistance

3.3.2.2.6 Heat Deformation referring to JIS K 6723

It is the percentage deformation of a sheet specimen of prescribed dimensions by a specified load at 120°C.

3.3.2.2.7 Dynamic Heat Stability

Dynamic heat test, the sample was not only thermally stressed but also subjected to shearing forces.(10) In this work, a continuous rolling test was used. PVC dry blend was prepared by using the formulation below.

UHMW PVC resin	100
Plasticizer (Dioctyl phthalate)	25
Stabilizer (Methyl tin mercaptide)	1.5
Internal lubricant (Glycerol monostearate)	2
Processing aid (Acrylic polymer)	2

The PVC dry blend was fused on a two-roll mill at a constant temperature of 200°C with the roll gap of 1 mm. It was subjected to continuous stress on the same mill. Every 5 minutes, the sample was taken from the center of the sheet which was then used for the assessment of color change.