

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of UHMW PVC Resin by Addition of Multiunsaturated Comonomer

From Table 4.1, UHMW PVC resin with  $\overline{DP}$  of  $2500 \pm 50$  can be obtained at  $40^{\circ}\text{C}$  without an addition of multiunsaturated comonomer.

As stated before, to keep the  $\overline{DP}$  of UHMW PVC resin at  $2500 \pm 50$  by polymerization at temperatures higher than  $40^{\circ}\text{C}$ , a multiunsaturated comonomer must be added. In this work, UHMW PVC resins with  $\overline{DP}$  of  $2500 \pm 50$  are produced at different polymerization temperatures of 43, 46, 49, 52 and  $58^{\circ}\text{C}$ . At each polymerization temperature, the amount of multiunsaturated comonomer is varied until the target  $\overline{DP}$  value is obtained. From the experiment, the amounts of multiunsaturated comonomer are 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 per hundred of VCM amount at 43, 46, 49, 52 and  $58^{\circ}\text{C}$ , respectively. The effects of comonomer amounts on  $\overline{DP}$  at each polymerization temperature are shown in Table 4.1.

At a given temperature,  $\overline{DP}$  increases with increasing the amount of comonomer as shown in Figs. 4.1-4.5. Since the comonomer, polyfunctional allyl ester, acts as a cross-linking agent,<sup>(4,7)</sup> the higher amount of cross-linking agent, the higher the ability to link each short chain of PVC together to result in a higher molecular weight of the PVC resin.

Table 4.1 : Effect of Comonomer on Degree of Polymerization at Different Polymerization Temperatures

Polyn. Temperature (°C)	Batch no.	Comonomer amount (phr)	Degree of polymerization
40	40-1	0	2490
	40-2	0	2500
43	43-1	0.000	2130
	43-2	0.010	2150
	43-3	0.040	2260
	43-4	0.055	2350
	43-5	0.075	2500
	43-6	0.075	2510
	43-7	0.100	2810
46	46-1	0.000	1880
	46-2	0.050	2080
	46-3	0.123	2540
	46-4	0.123	2540
	46-5	0.200	4000
49	49-1	0.000	1590
	49-2	0.100	1930
	49-3	0.160	2400
	49-4	0.166	2530
	49-5	0.166	2550
	49-6	0.175	2780
	49-7	0.250	3550
52	52-1	0.000	1370
	52-2	0.200	2540
	52-3	0.200	2540
	52-4	0.220	2980
	52-5	0.300	4220
58	58-1	0.000	1020
	58-2	0.270	2380
	58-3	0.280	2510
	58-4	0.280	2530
	58-5	0.310	2800

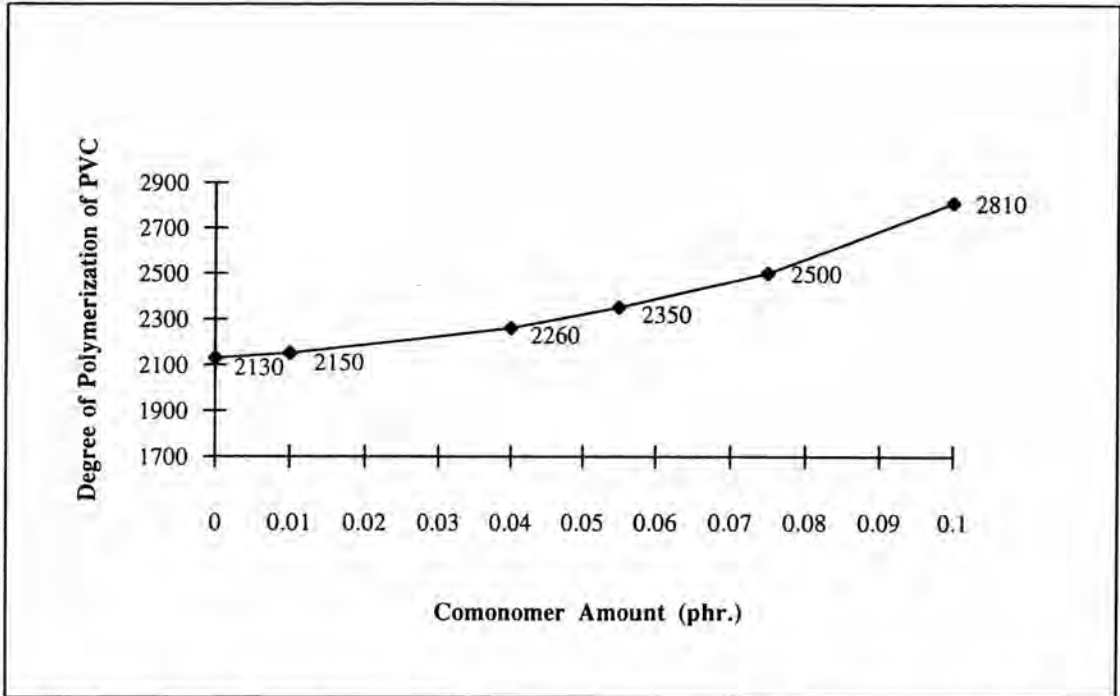


Fig. 4.1 : Effect of Comonomer Amount on Degree of Polymerization of PVC at the Polymerization Temperature of 43°C

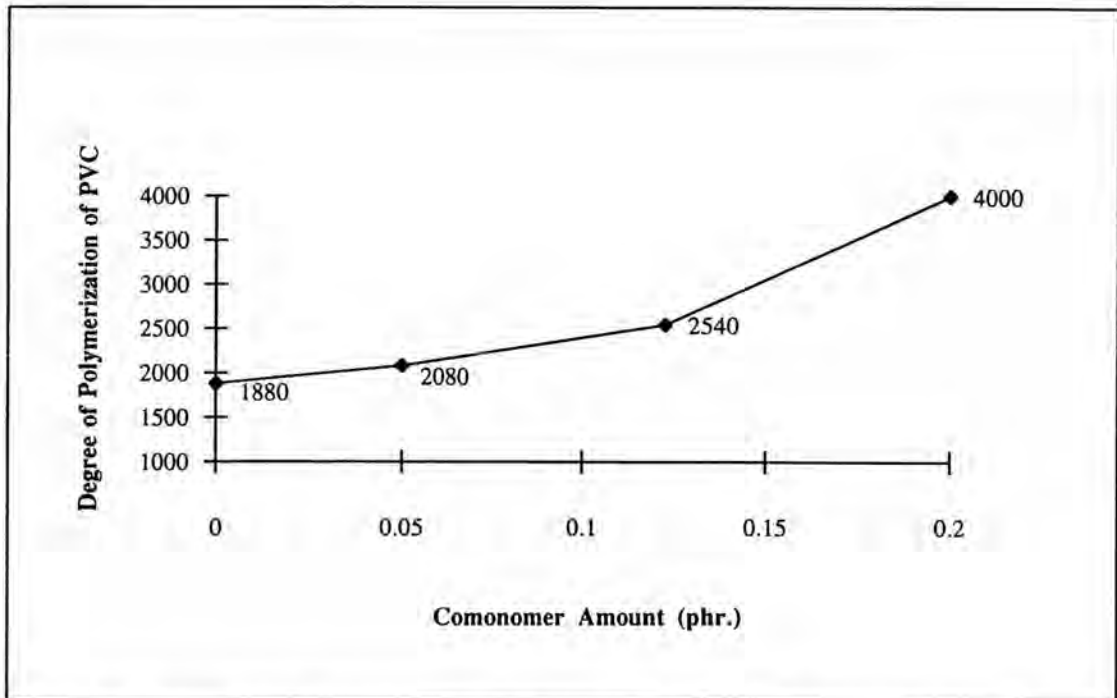


Fig. 4.2 : Effect of Comonomer Amount on Degree of Polymerization of PVC at the Polymerization Temperature of 46°C

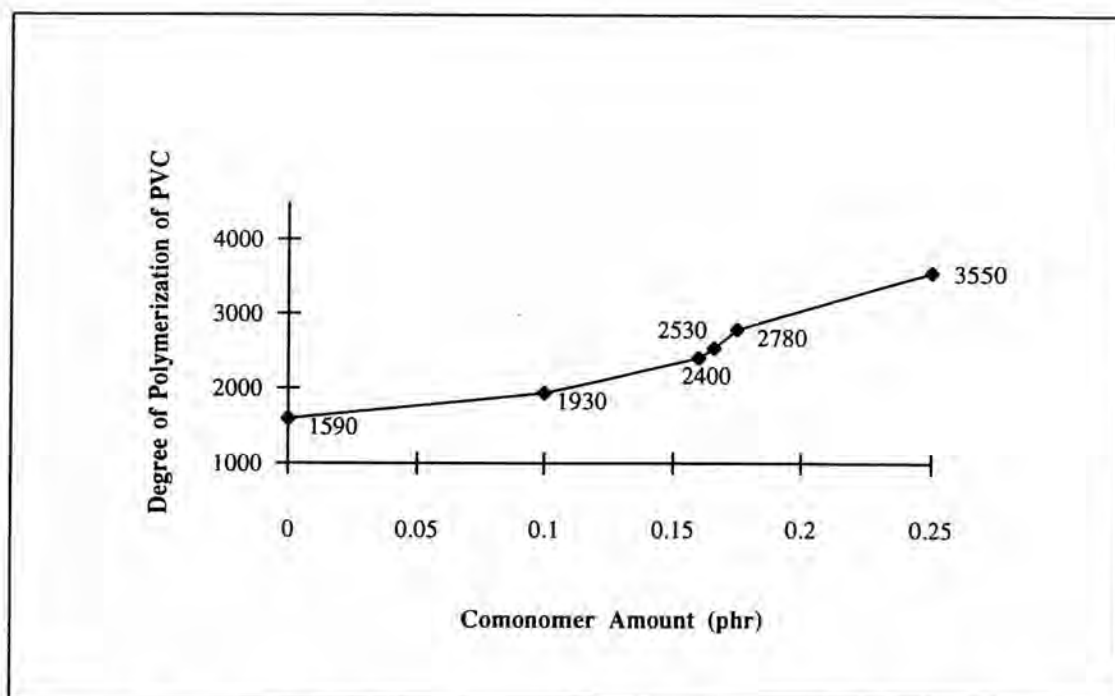


Fig. 4.3 : Effect of Comonomer Amount on Degree of Polymerization of PVC at the Polymerization Temperature of 49°C

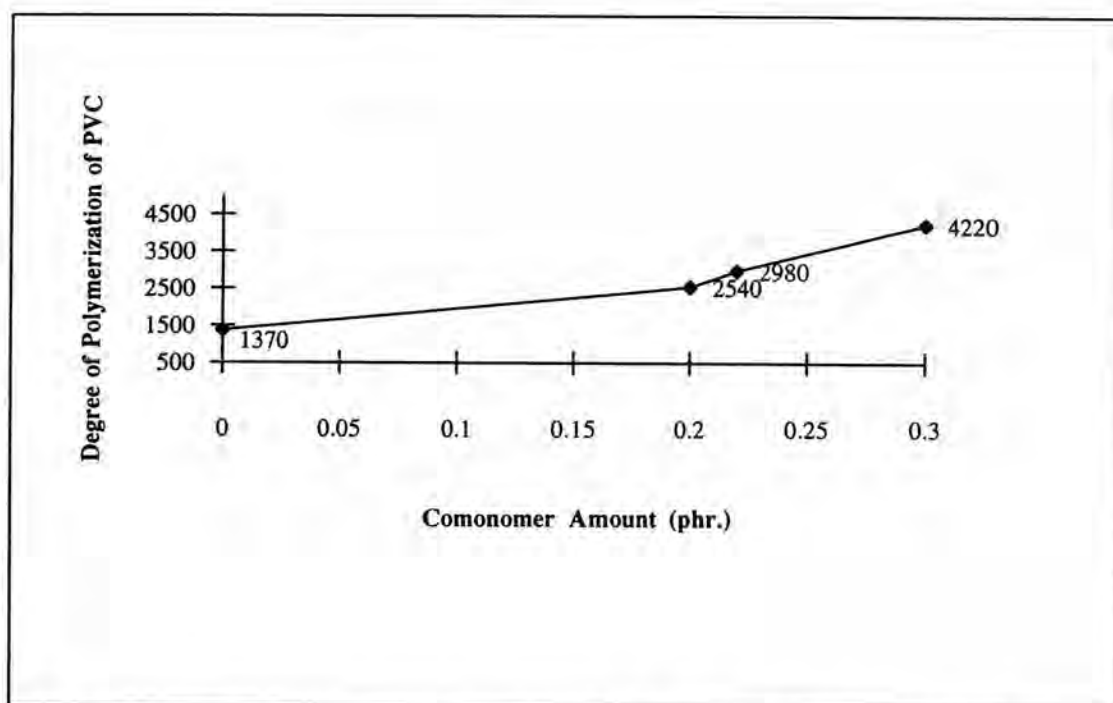


Fig. 4.4 : Effect of Comonomer Amount on Degree of Polymerization of PVC at the Polymerization Temperature of 52°C

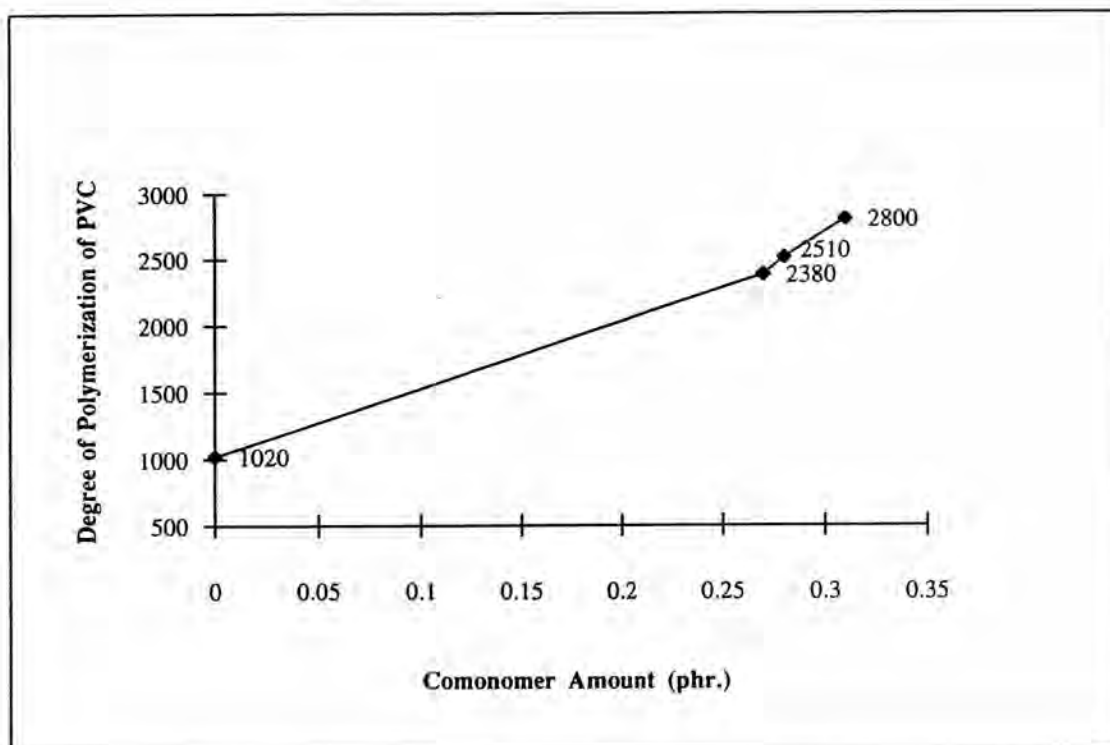


Fig. 4.5 : Effect of Comonomer Amount on Degree of Polymerization of PVC at the Polymerization Temperature of 58°C

At different polymerization temperatures, a given  $\overline{DP}$  of UHMW PVC resin can be obtained by increasing the comonomer amount with increasing polymerization temperature as shown in Table 4.2 and Fig. 4.6. In the absence of other reactive agents, the molecular weight of PVC is controlled by the chain transfer to monomer which the rate constant of chain transfer reaction depends on the temperature from Arrhenius equation therefore the molecular weight of PVC resin is almost controlled by the polymerization temperature.<sup>(2,6,11)</sup> The higher polymerization temperature offers a lower  $\overline{DP}$  or a shorter chain of PVC molecules. Thus the higher temperature polymerization needs more cross-linking agents to link many shorter PVC chains produced by a large amount of initiator radicals to give a greater number of short kinetic chains, to become longer or larger molecules similarly to the lower temperature polymerizations.

Table 4.2 : Relation between Polymerization Temperature and Comonomer Amount at  $\overline{DP}$  between 2450 to 2550

Polymerization temperature ( $^{\circ}\text{C}$ )	Comonomer amount (phr.)
40	0.000
43	0.075
46	0.123
49	0.166
52	0.200
58	0.280

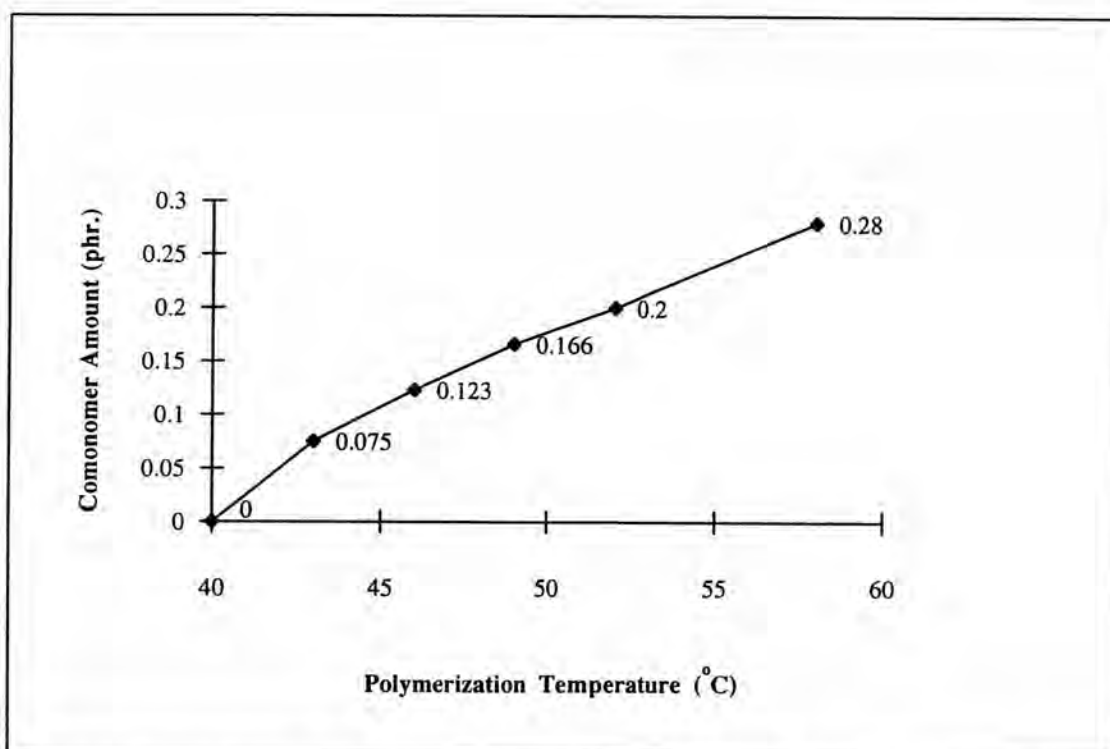


Fig. 4.6 : Relation between Polymerization Temperature and Comonomer Amount

The longer or larger molecules, the higher molecular weights, and the higher the  $\overline{DP}$  values. The relation between comonomer amount and the reaction time at each polymerization temperature is shown in Appendix C.

## **4.2 Effect of Multiunsaturated Comonomer Amount on Properties of UHMW PVC**

UHMW PVC resins with  $\overline{DP}$  of  $2500 \pm 50$  from Table 4.1 were investigated for the properties in comparison with the reference UHMW PVC resin, the properties of UHMW PVC resin and the properties of UHMW PVC dry blend.

### **4.2.1 Properties of UHMW PVC Resin**

All the results are shown in Table 4.3.

#### **1. Mean Particle Size**

From the results, the particle size of all UHMW PVC resins are in the range of 122-132 micrometers which are not significantly different. Thus there is no obvious effect of multiunsaturated comonomer amount on particle size of UHMW PVC resin. The particle size of PVC is controlled by the agitation speed and suspending agent used. The polymerization monomer droplets in the suspension polymerization are formed and stabilized by the combined effect of vigorous agitation and the presence of suspending agent.<sup>(11)</sup> The agitation provides the mechanical energy to disperse monomer into droplets, the droplet size decreases as the agitator speed increases. Without a continuous agitation, the polymerization mixture would separate into a water phase and monomer phase. In case of suspending agent, their functions are to control the interparticle and intraparticle agglomeration in



Table 4.3 : Effect of Comonomer Amount on Resin Properties of UHMW

PVC

Property	Unit	Comonomer amount (phr.)					
		0.000	0.075	0.123	0.166	0.200	0.280
Mean particle size	micrometer	128	130	132	124	122	129
Size distribution coefficient		0.26	0.28	0.28	0.3	0.31	0.32
Bulk density	g/mL	0.36	0.35	0.35	0.35	0.34	0.35
Cold plasticizer absorption	%	34.8	30.6	30.1	28.3	26.3	24.3
Fisheye	points	27	43	36	36	47	43
Moisture content	%	0.2	0.3	0.2	0.2	0.2	0.2

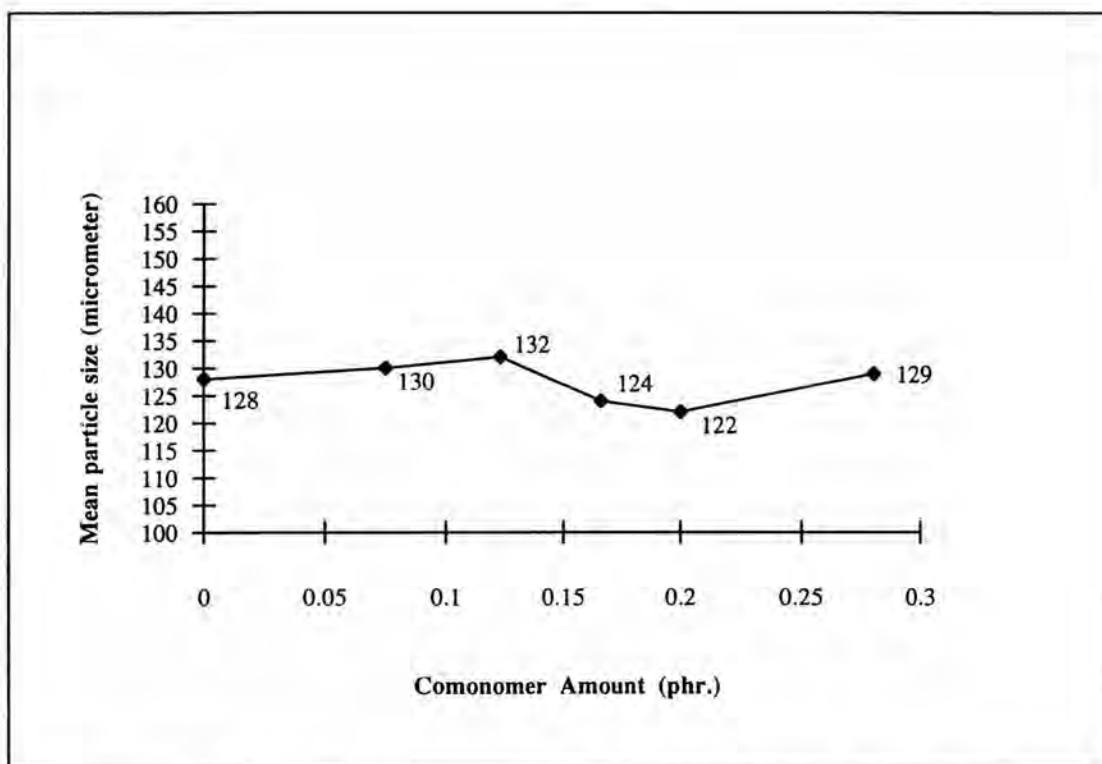


Fig. 4.7 : Effect of Comonomer Amount on Mean Particle Size of UHMW

PVC Resin



the PVC grains<sup>(2)</sup> by gravitating to the interface between the monomer and aqueous phases stabilizing the droplets by lowering the interfacial tension between the two phases.<sup>(6)</sup> The interparticle agglomeration will determine the particle size and the particle size distribution for the PVC resin and the intraparticle agglomeration will control the bulk density and porosity of the resin.

In this work, both agitator speed and mixed suspending agents are controlled to the same level for each polymerization. Thus mean particle size of all UHMW PVC resins is nearly constant as shown in Fig. 4.7.

## **2. Size Distribution Coefficient**

Size distribution coefficient tends to increase with increase of comonomer amount as shown in Fig. 4.8. This might be the result of higher polymerization temperature which would affect solubility of suspending agents. Since the suspending agent of the partially hydrolyzed poly(vinyl alcohol) precipitates at elevated temperatures and its efficiency is slightly decreased.<sup>(12)</sup> Such a small decrease in solubility does not affect the mean particle size due to the stable droplets of VCM. However, size distribution coefficient can be improved by using other suspending system, which is suitable for each polymerization temperature.

## **3. Bulk Density**

Likewise, there is no significant effect of comonomer amount on bulk density of UHMW PVC resins as shown in Fig. 4.9. In general, this property is influenced by the suspending agent used and water to VCM ratio. If suspending agents used cannot stabilize the intraparticle agglomeration, the bulk density would be increased as a result of low porosity<sup>(2)</sup>

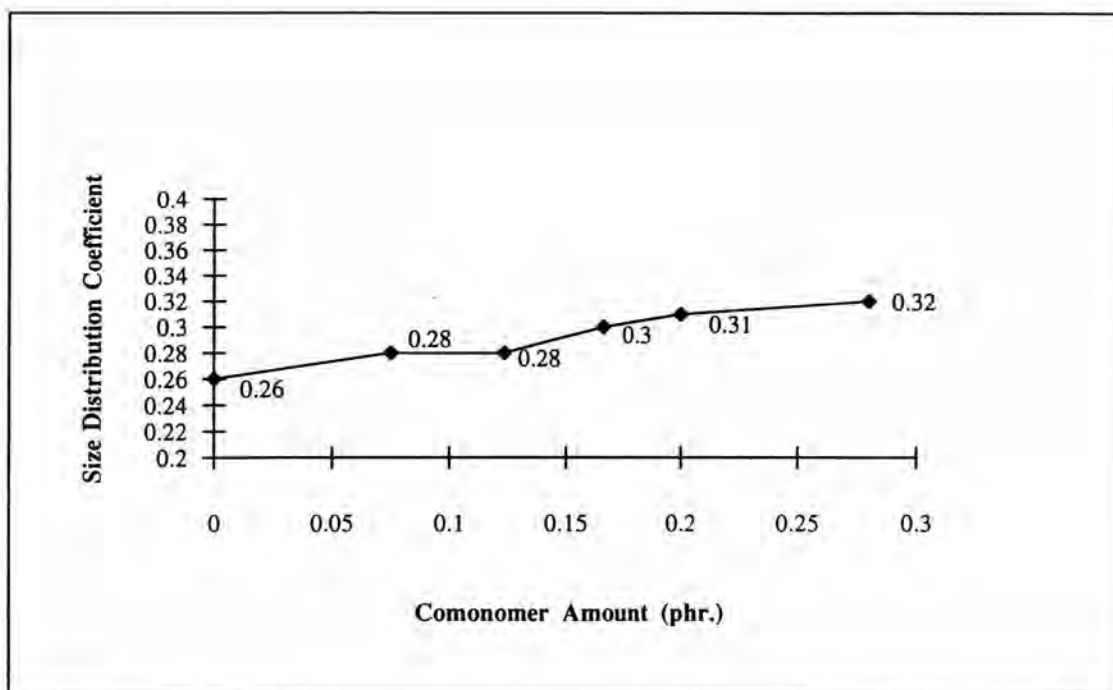


Fig. 4.8 : Effect of Comonomer Amount on Size Distribution Coefficient of UHMW PVC Resin

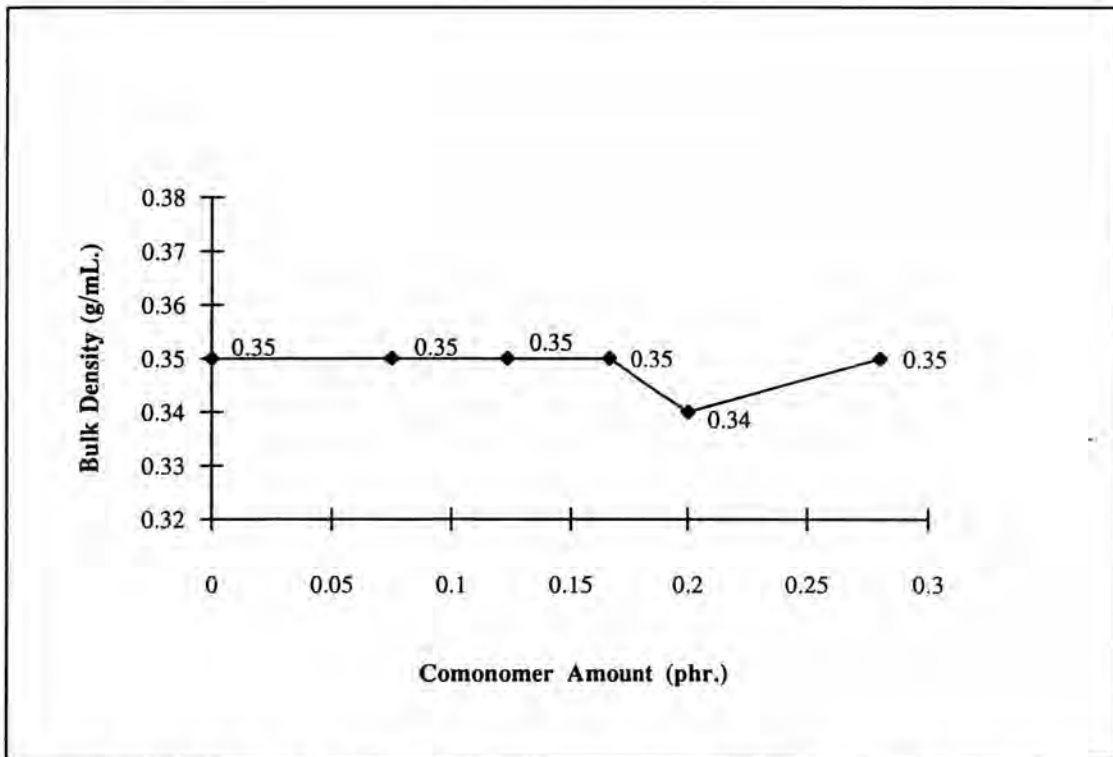


Fig. 4.9 : Effect of Comonomer Amount on Bulk Density of UHMW PVC Resin

The bulk density in this work is constant although the porosity decreases. The possible reason is that they may be closed pores in the lower porosity resin. These closed pores cannot be detected by the cold plasticizer absorption method. Only those pores open to the outside of the resin are filled with plasticizers.<sup>(11)</sup> Thus CPA result of the present work shows the lower value than those containing actual pores. With more closed pores in PVC particles the lower bulk density would be found in the PVC resin.

In case of water-to-VCM ratio, increasing this ratio decreases the bulk density. Suspension polymerization requires a large quantity of water to act as a continuous phase to break the VCM to discrete droplets by agitation; to act as a heat transfer medium, and as a carrier for the suspending agent.<sup>(6)</sup> The water that acts as a continuous phase fills all the spaces of the dispersed droplets. These spaces become voids in PVC particles after drying. Thus increasing water-to-VCM ratio results in the higher porosity or the lower bulk density.

#### **4. Cold Plasticizer Absorption (CPA)**

The most important property of UHMW PVC is the capability of PVC grains to absorbing a number of different substances such as stabilizers, lubricants, fillers and pigments.<sup>(10)</sup> For flexible applications the PVC grains must be able to absorb large quantities of plasticizers homogeneously during the blending stage. The aim is to obtain dry free flowing mixtures (dry blend) in a short cycle time which can be subsequently processed into, for example, cable covering free from surface defects. All of the applications require PVC grains with some degree of porosity as measured by cold plasticizer absorption.<sup>(13)</sup> For a given set of polymerization condition, the

polymerization temperature imposes a very large effect on PVC porosity.<sup>(11)</sup> As shown in Fig. 4.10, porosity decreases with increasing polymerization temperature. At a high polymerization temperature, the polymerization rate is correspondingly high to influence the rate of primary particle growth: i.e. high growth rates before collisions with other primary particles taking place to form agglomerates without any conglomeraiton. These primary particles are usually solid spheres with no sub-structure that result in low porosity.<sup>(11)</sup>

### 5. Fisheye

Fisheyes are resin particles which have not been fused under a given set of processing (or testing) conditions. They often appear as translucent particles in finished product, because they are in the absence of compound ingredients such as plasticizer during blending and processing. However, fisheyes in plasticized PVC are usually caused by oversized or nonporous particles formed during polymerization.<sup>(10)</sup> The particle morphology of PVC resin is not wholly uniform in a large population sample. It has been estimated that for a typical resin sample approximately one particle in about  $10^5$  particles will have a low porosity and a slow rate of plasticizer absorption.<sup>(2)</sup> These low plasticizer absorbing particles will result in fisheyes in a flexible film.

All the PVC products which used the comonomer gave slightly poorer fisheyes than the reference product are shown in Fig. 4.11. The cause of low porosity or poorer plasticizer absorption is due to the higher polymerization temperature.<sup>(11)</sup> However, this problem could not be affected directly by the comonomer used, but it was indeed affected by the polymerization temperature.

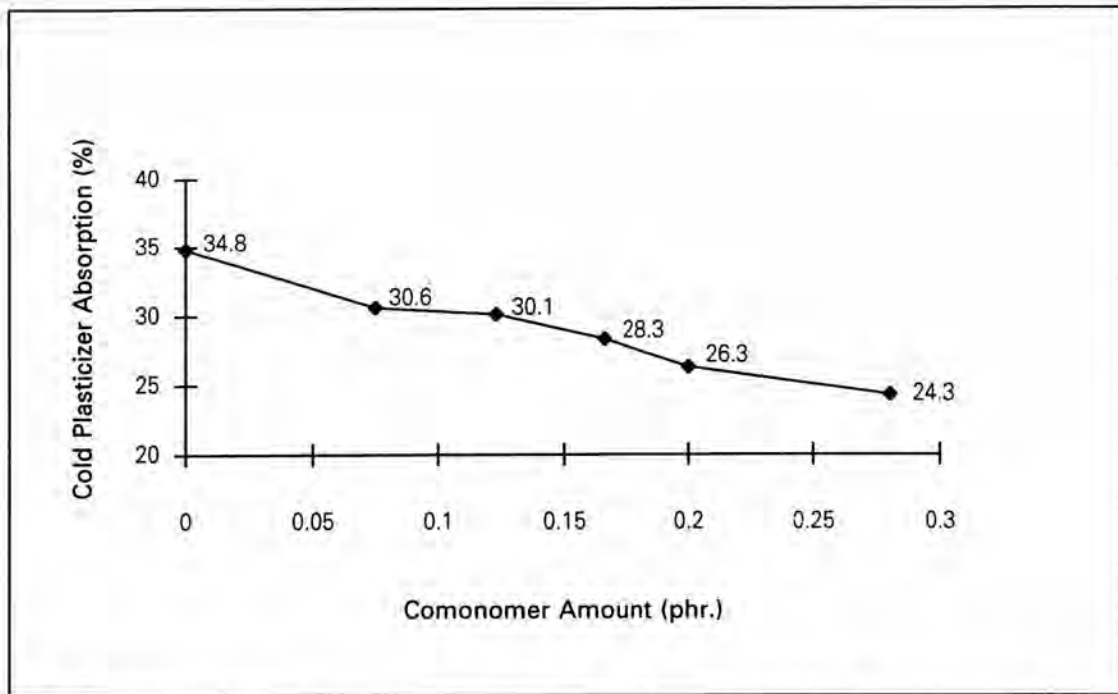


Fig. 4.10 : Effect of Comonomer Amount on Cold Plasticizer Absorption of UHMW PVC Resin

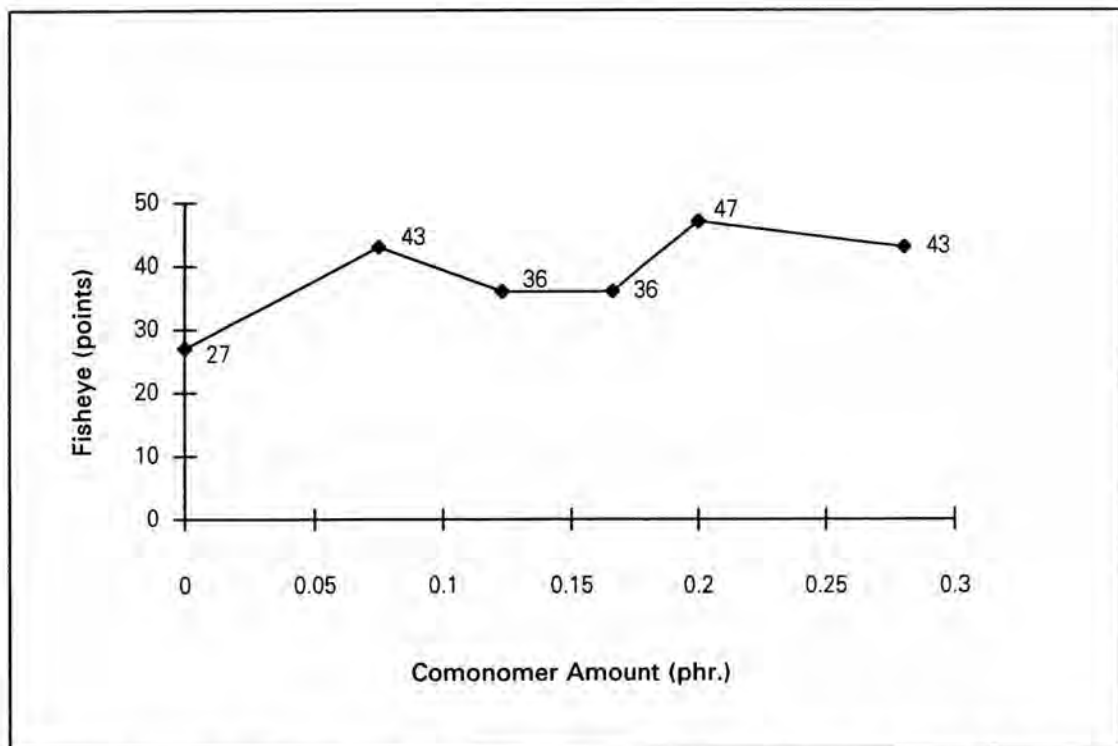


Fig. 4.11 : Effect of Comonomer Amount on Fisheye of UHMW PVC Resin

However, it is not a serious problem at all, since the porosity can be improved by adjusting the formulation of polymerization.

#### 4.2.2 Properties of Dry Blend of UHMW PVC Resins

All the properties are shown in Table 4.4.

##### 1. Hardness

In general, plasticization reduces the hardness of high molecular materials. The efficiency of plasticizing substances is specific to the type of plasticizer, the quantity used, and the temperature<sup>(14)</sup> which are controlled to the same level during the test. For cable compounds, the acceptable hardness range is  $X \pm 3$ , where  $X$  is the reference hardness value. In this work, the reference hardness value which is the hardness of UHMW PVC, without an addition of comonomer, is 76 to produce the acceptable hardness range of  $76 \pm 3$ . As the result shown in Fig. 4.12, the hardness slightly decreases with an increase of comonomer amount. Although they are in the acceptable hardness range, they may be slightly affected due to low trend values. As mentioned earlier, porosity decreases with increases of comonomer amount and decreases of hardness.

At the same amount of plasticizer, it may be sufficient for high porous PVC but excess for low porous PVC. Since a dry blend of low porous PVC looks wet with plasticizer. Most plasticizers have limits of compatibility with PVC. The plasticizer works when it is sufficiently compatible to maintain the desired polymer-plasticizer interaction, including the presence of other additives which influence the compatibility of the total plasticized PVC system<sup>(14)</sup>. If the plasticizer amount is not optimized for low porous PVC, the excess plasticizer would migrate to the surface of PVC product. This migration



Table 4.4 : Effect of Comonomer Amount on Dry Blend Properties of UHMW PVC

Property	Unit		Comonomer amount (phr.)					
			0	0.075	0.123	0.166	0.200	0.280
Hardness (Shore A, 15 sec.)		ave.	76	76	75	74	74	73
		SD	1.0	0.5	0.5	0.5	0.5	0.0
Tensile strength	N/mm <sup>2</sup>	ave.	25.19	23.54	22.97	22.25	21.14	19.49
		SD	0.10	0.18	0.09	0.10	0.25	0.14
Elongation	%	ave.	328	335	348	355	365	393
		SD	2.5	15.0	2.5	5.0	15.0	17.5
Brittleness temperature	°C	ave.	-35	-35	-34	-35	-35	-34
		SD	1.0	1.5	1.0	0.5	1.0	1.0
Volume resistivity	x10 <sup>5</sup> MΩm	ave.	2.25	3.65	5.54	4.03	4.73	10.81
	x 10 <sup>4</sup>	SD	0.19	0.04	0.05	0.03	0.04	1.40
Heat deformtion	%	ave.	4.07	4.30	4.49	6.48	6.71	7.72
		SD	0.06	0.04	0.02	0.04	0.02	0.03
Dynamic heat stability -Burnt time	min.		45	60	60	60	65	65



is termed exudation or bloom since the appearance of the deposit is wet or oily looking.<sup>(15)</sup> However, hardness values of all UHMW PVC are in the acceptable range which may be the result of having the same molecular weight.

## 2. Tensile Strength

The result in Fig. 4.13 indicates that tensile strength decreases with increase of comonomer amount. The possible reasons are more free volume and lower syndiotactic level in the structure. The free volume is the free space between molecules. It increases with increasing the molecular motion. Increasing the concentration of chain ends increases the free volume. Therefore, decreasing the molecular weight of a polymer increases free volume, which is end-group plasticization.<sup>(2)</sup> When PVC polymerization is being proceed, the lower molecular weight PVC is produced at higher polymerization temperatures. In this work, the UHMW PVC which produced at the highest polymerization temperature offers the lowest tensile strength and its molecular weight is controlled by addition of comonomer. Addition of some side chains produces the same result<sup>(2)</sup> as comonomer addition in this work; the higher the polymerization temperature, the higher the amount of comonomer can control the molecular weight at the specified level. The sample polymerized at 58°C with the highest amount of comonomer offers the lowest tensile strength. Enough free volume permits a freedom of movement as if there are holes for nearby atoms or chain segments to move into. The normal result of adding more free volume to a polymer is to plasticize the polymer. Its  $T_g$  becomes lower; the modulus and tensile strength decrease, but its impact strength and elongation increase.<sup>(2)</sup>

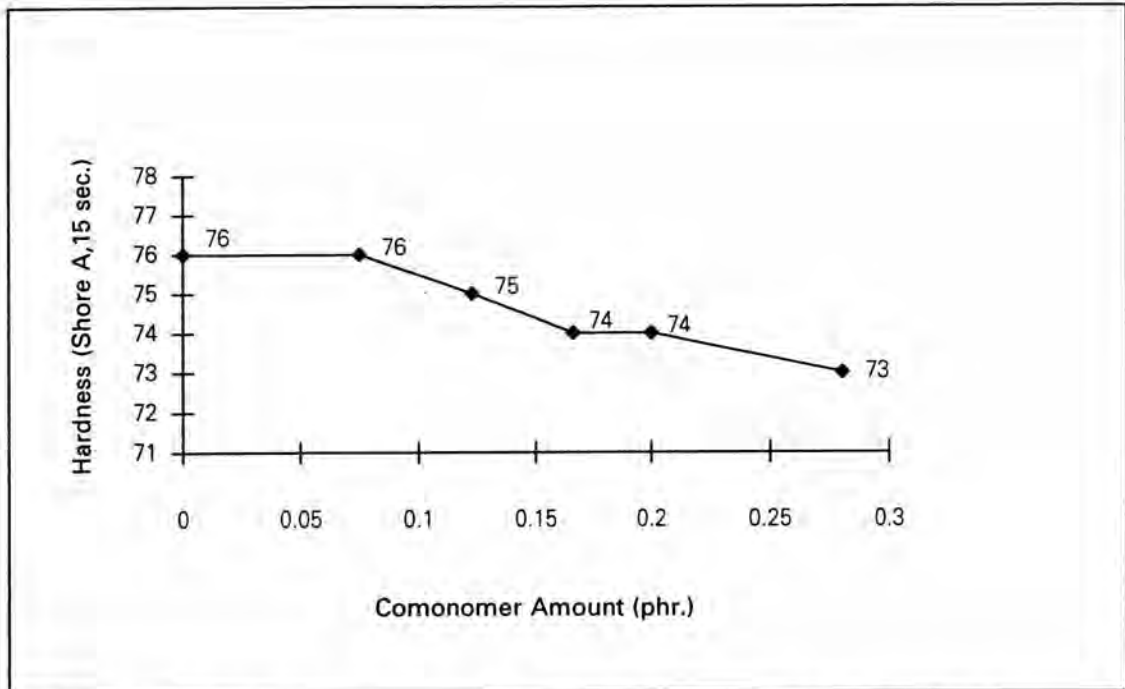


Fig. 4.12 : Effect of Comonomer Amount on Hardness of UHMW PVC Dry Blend

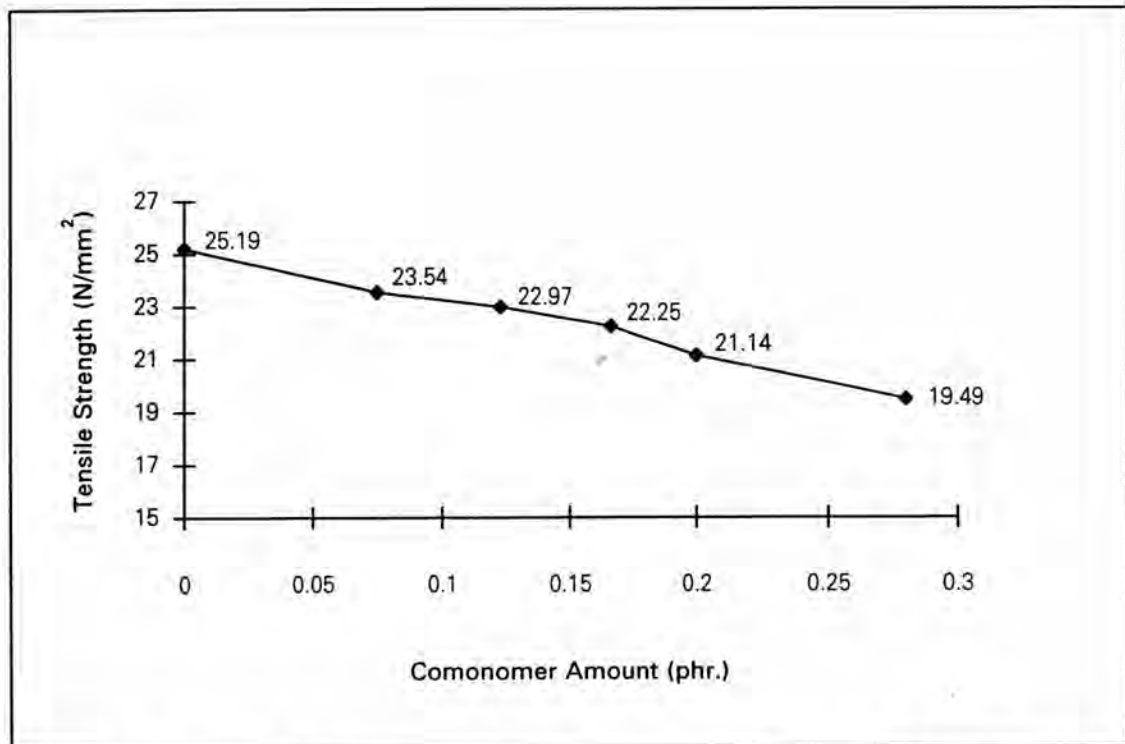


Fig. 4.13 : Effect of Comonomer Amount on Tensile Strength of UHMW PVC Dry Blend

PVC synthesized by a free-radical initiation, has a low level of crystallinity of about 10% for the PVC prepared in the range 45 to 75°C. As the polymerization temperature is decreased, the percent crystallinity relatively increases and such an increase in crystallinity has been related to the increase in syndiotacticity in PVC. There is a linear relationship between the level of syndiotacticity and polymerization temperature as shown in Fig. 4.14.<sup>(2,9)</sup> PVC with high syndiotacticity and crystallinity produces high tensile strength.<sup>(2)</sup> In this work, the UHMW PVC produced at the lowest temperature gives the highest tensile strength, which is believed to be caused by the higher crystallinity.

### 3. Elongation

The result in Fig. 4.15 indicates that elongation increases with increase of comonomer amount. This property relates to tensile strength. Increasing the tensile strength decreases elongation. In this work, the UHMW PVC with the highest amount of comonomer should have more chain ends and side chains, which result in the freedom of chain movement. Thus  $T_g$  becomes lower; the tensile strength decreases but elongation increases.<sup>(2)</sup> In case of tacticity of PVC, highly crystalline PVC with high syndiotactic content has been prepared by polymerization at low temperatures<sup>(9)</sup> therefore the UHMW PVC prepared at the lowest polymerization temperature can give the highest tensile strength and the lowest elongation.

### 4. Brittleness Temperature

The result in Fig. 4.16 indicates that comonomer does not affect brittleness temperature of UHMW PVC at all. Normally this property is influenced by glass transition temperature  $T_g$  of PVC; the higher the  $T_g$ , the

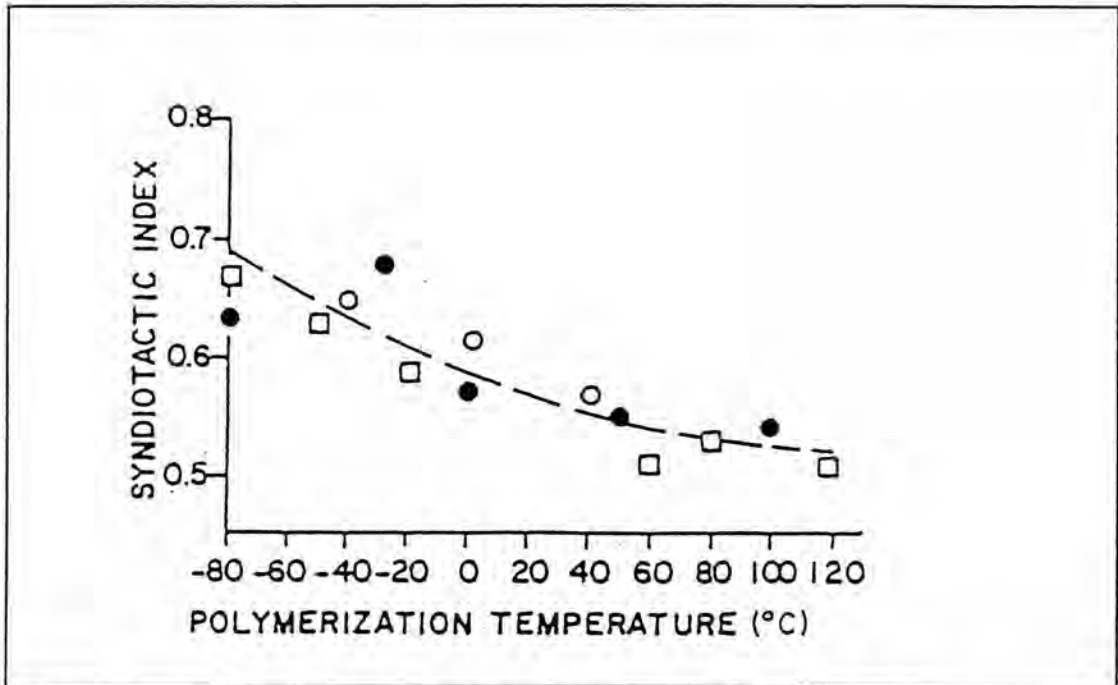


Fig. 4.14 : Relation between Syndiotactic Index and Polymerization Temperature<sup>(2)</sup> (different symbols mean different polymerization processes)

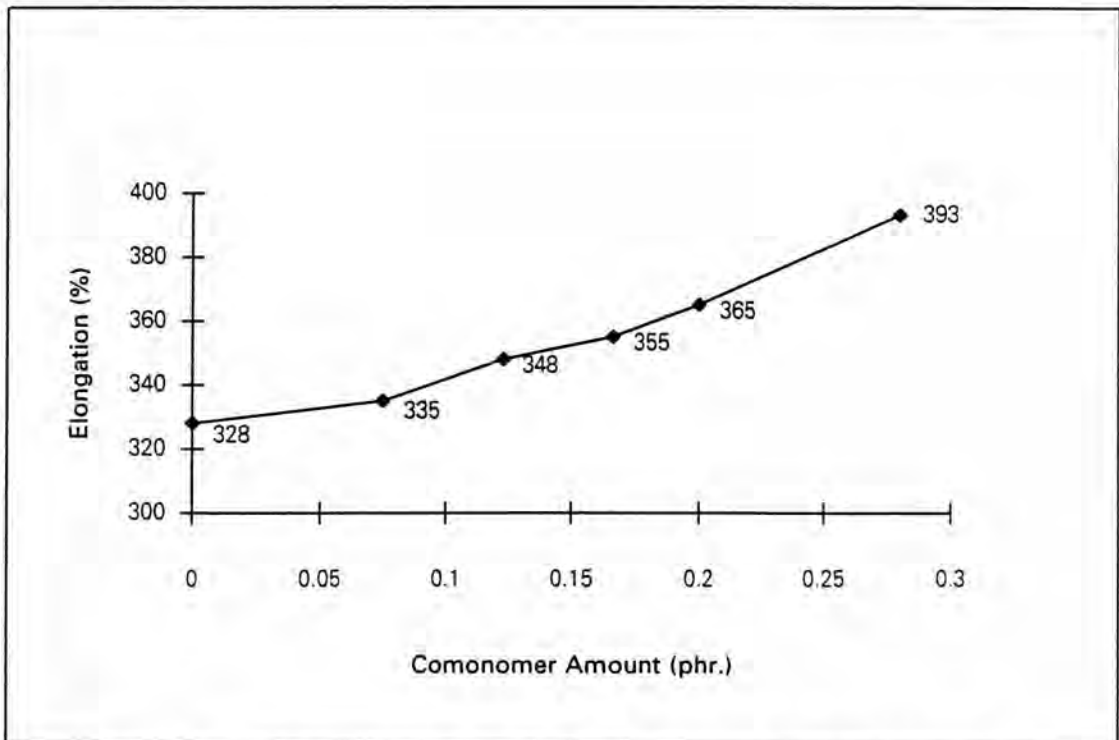


Fig. 4.15 : Effect of Comonomer Amount on Elongation of UHMW PVC Dry Blend

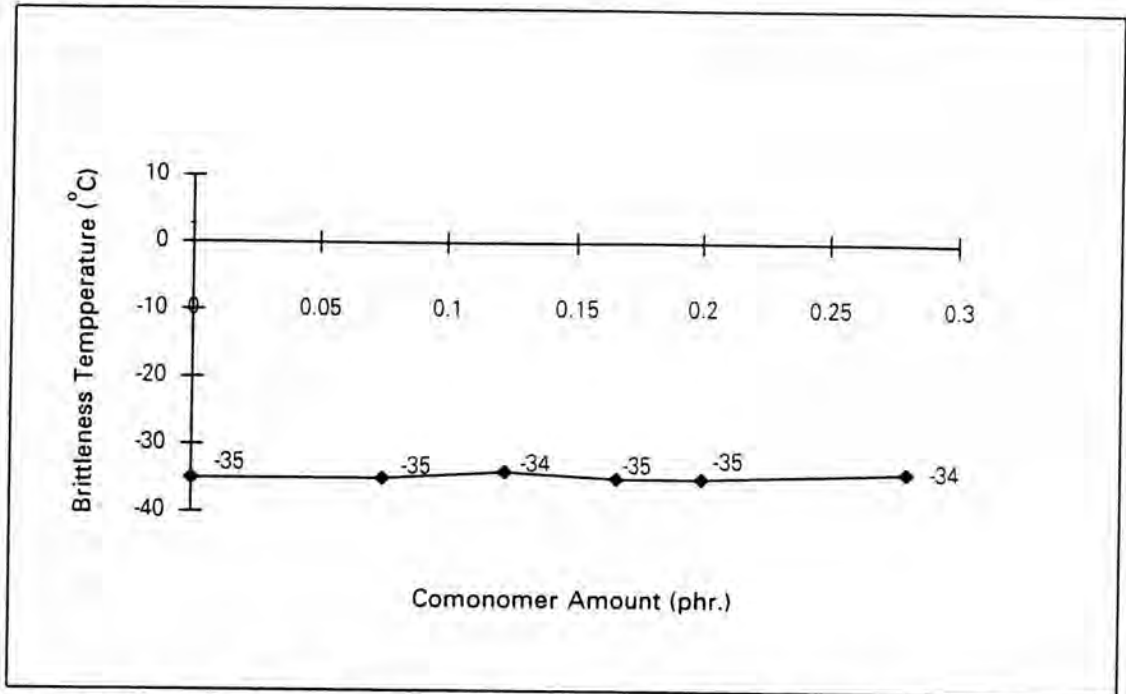


Fig. 4.16 : Effect of Comonomer Amount on Brittleness Temperature of UHMW PVC Dry Blend

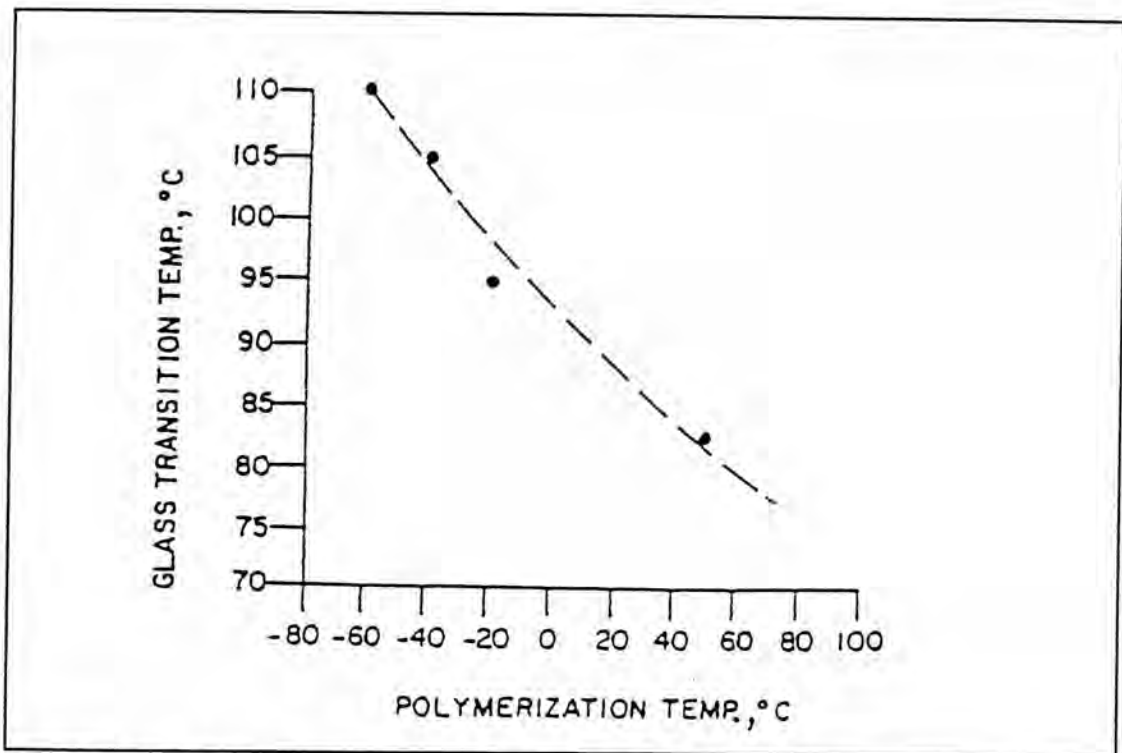


Fig. 4.17 : Relation between Glass Transition Temperature and Polymerization Temperature<sup>(2)</sup>

higher the brittleness temperature. As shown in Fig. 4.17 the  $T_g$  of PVC varies with the temperature of polymerization, in practice, all commercially available resins having  $T_g$  values between 80 and 85°C. As polymerization temperature is the main controlling factor for molecular weight,  $T_g$  is thus directly related to molecular weight.<sup>(2)</sup> In this work, the brittleness temperatures are compared between UHMW PVCs with different comonomer amounts at the same molecular weight. Another factor which effects on  $T_g$  is type and concentration of the plasticizer used. Since thermoplastics are in a brittle state below their glass temperature, plasticizer shifts down the  $T_g$  as it moves into the amorphous regions of the polymer grains which can reduce polymer-polymer interaction forces.<sup>(15)</sup> In this work, type and concentration of the plasticizer are controlled to the same degree for every sample. Thus there is no significant effect of comonomer on the brittleness temperature of UHMW PVC, although the hardness and heat deformation related to this property are affected.

### 5. Volume Resistivity

The result shown in Fig. 4.18 indicates that volume resistivity is improved with comonomer addition. This is the result of decreasing polarity of UHMW PVC and comonomer itself since the polymer of diallyl ester used in the application requires heat resistance and good electrical resistivity.<sup>(7)</sup>

### 6. Heat Deformation

Under a specified load at 120°C, UHMW PVC samples are deformed. This property is influenced by hardness, the lower the hardness, the higher the deformation. The result in Fig. 4.19 indicates that percentage of heat deformation increases with increases of comonomer amount. This is the result

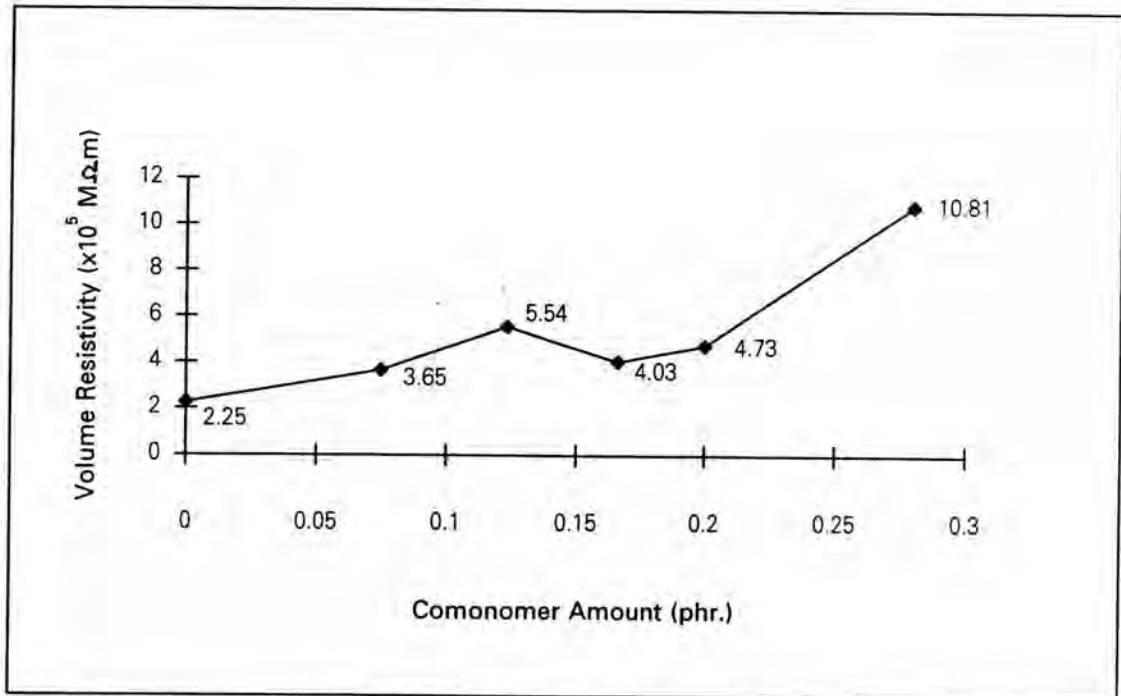


Fig. 4.18 : Effect of Comonomer Amount on Volume Resistivity of UHMW PVC Dry Blend

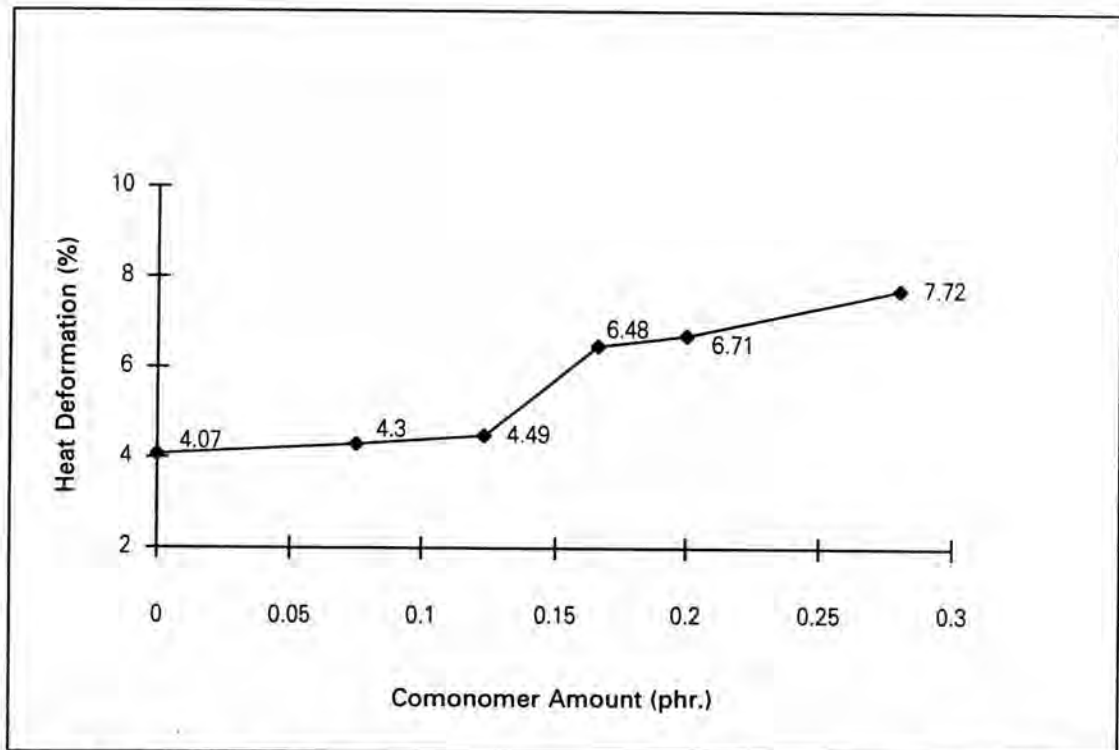


Fig. 4.19 : Effect of Comonomer Amount on Heat Deformation of UHMW PVC Dry Blend



of lower hardness of the sample which used more comonomer amount. This value does not detect the resilience of PVC since it is detected under the loading at specified temperature. Beside the hardness, the percentage of heat deformation relates to elongation also presented as the results in Table 4.4, heat deformation increases with increasing elongation.

### 7. Dynamic Heat Stability

The results shown in Figs. 4.20 and 4.21 indicate that dynamic heat stability of the reference UHMW PVC is poorer than that of UHMW PVC with an addition of the comonomer. But the comonomer amount does not significant affect dynamic heat stability.

Concentration and type of polymerization residue can affect the heat stability.<sup>(12)</sup> From the polymerization formulations in Appendix A, the suspending agent is controlled to the same level in every polymerization batch and temperature, only the initiator amount is decreased with increases of polymerization temperature. The reference UHMW PVC was polymerized with the highest amount of initiator. This may have more initiator residues in the PVC obtained, which result in a poorer heat stability. Since the initiator is an active substance, it can be activated by heat or light to initiate undesirable reactions which result in poorer heat stability. Another reason is the result of comonomer itself since the diallyl esters can act as stabilizers against oxidative degradation and heat discoloration thus it can improve the dynamic heat stability of the UHMW PVC. Moreover, the polymer with this comonomer is used in the application which requires heat resistance and electrical resistivity<sup>(7)</sup> The amounts of comonomer between 0.075 to 0.280 phr. give a constant heat stability. This may be due to that the disadvantage of higher heat history from

the higher polymerization temperature is compensated by higher amounts of the comonomer.

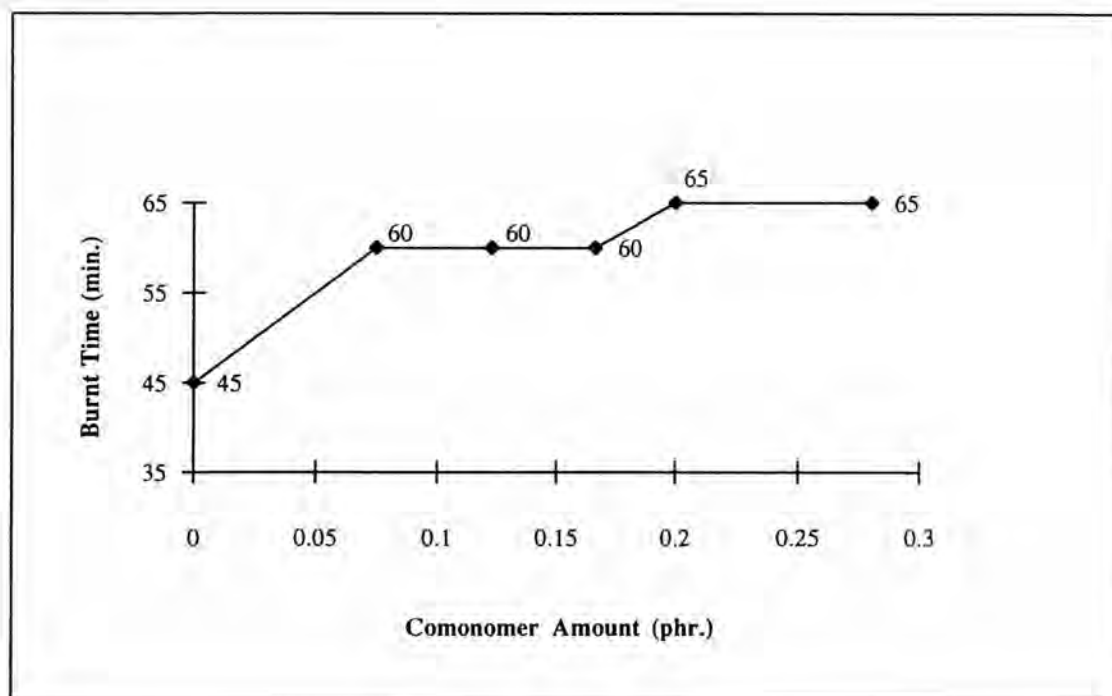


Fig. 4.20 : Effect of Comonomer Amount on Dynamic Heat Stability of UHMW PVC Dry Blend

## CONTINUOUS ROLLING TEST

ROLL TEMPERATURE

200°C

ROLL GAP 1 mm.

TIME (min.)	Comonomer amount (phr.)					
	0.000	0.075	0.123	0.166	0.200	0.280
5						
10						
15						
20						
25						
30						
35						
40						
45						
50						
55						
60						
65						

Fig. 4.21 : Result of Dynamic Heat Stability