CHARTER IV

RESULTS AND DISCUSSION

4.1 Preparation of Low Molecular Weight PVC Resin without Chain Transfer Agent

To study the effect of temperature on the K-value of low molecular weight PVC resin by polymerization at high temperature without using chain transfer agent, the polymerization temperature was varied from 69 to 82°C.

Figure 4.1 shows the relationship between polymerization temperature and K-value. It could be seen that the K-value of PVC resin decreased as the polymerization temperature increased. The required K-value of 50 was obtained at 81°C

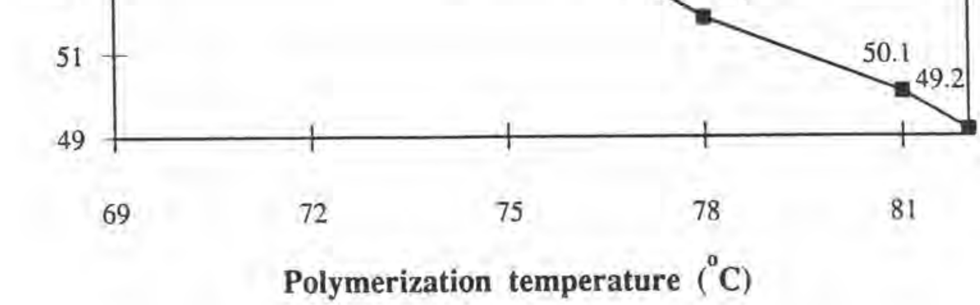

Figure 4.1 Relationship between polymerization temperature and K-value

4.2 Preparation of Low Molecular Weight PVC Resin in the Presence of Chain Transfer Agent.

The preparation of PVC resin depends on the polymerization temperature. As the polymerization temperature becomes higher, the molecular weight of PVC decreases or short chain of PVC is obtained. While lower polymerization temperature gives high molecular weight PVC.(3) In order to prepare low molecular weight PVC resin at low temperature, addition of chain transfer agent is necessary. Larger amount of the chain transfer agent is needed for the lower polymerization temperature.

This study focused on the effect of chain transfer agent. The polymerization temperature employed were 69, 73 and 77°C and the amount of chain transfer agent was varied in each polymerization temperature until the target K-value of 50 was obtained.

Figures 4.2 - 4.4 show the relationship between chain transfer agent dosage and K-value at the polymerization temperature of 77, 73 and 69°C. It was found that the K-value of PVC resin decreased as the amount of chain transfer agent increased. To obtain PVC resin with K-value of 50 at the polymerization temperature of 77, 73 and 69°C, the optimum amount of chain transfer agent needed were 0.027, 0.047 and 0.080 phm, respectively.

In this study, mercapto-containing organic compound was used as a chain transfer agent. As the amount of chain transfer agent was increased, the polymerization rate decreased. Therefore, the amount of initiator was adjusted in each polymerization to fix the polymerization time at 5 hours.

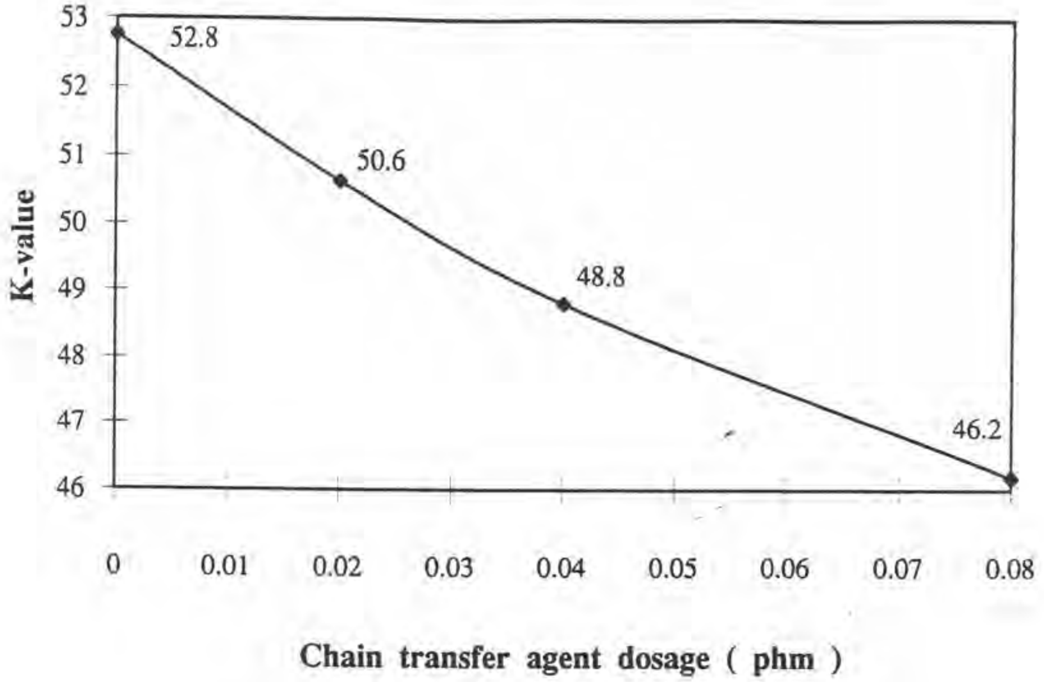

Figure 4.2 Relationship between chain transfer agent dosage and K-value at the polymerization temperature of 77°C

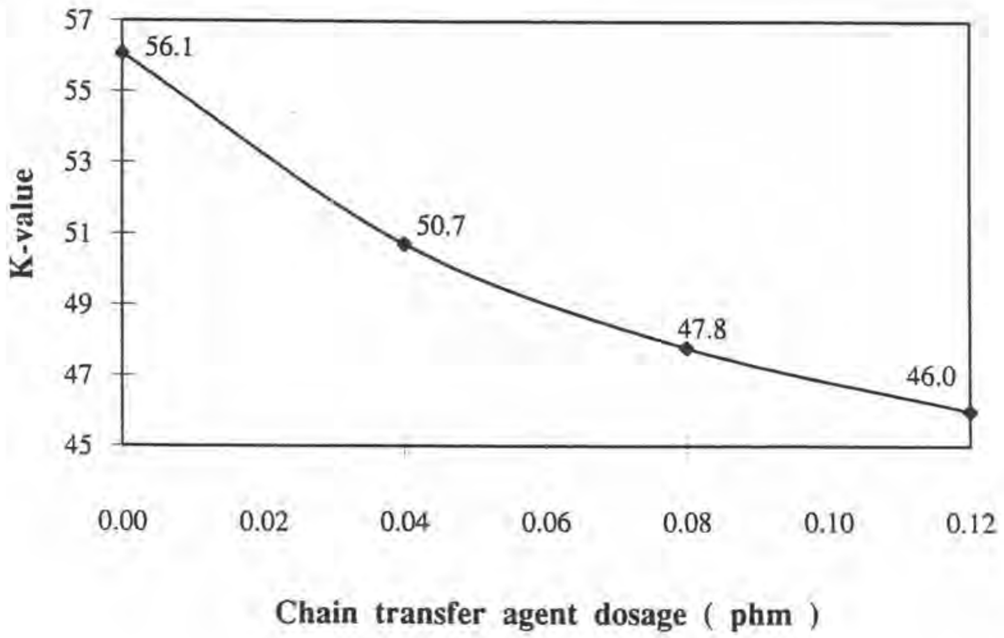

Figure 4.3 Relationship between chain transfer agent dosage and K-value at the polymerization temperature of 73°C

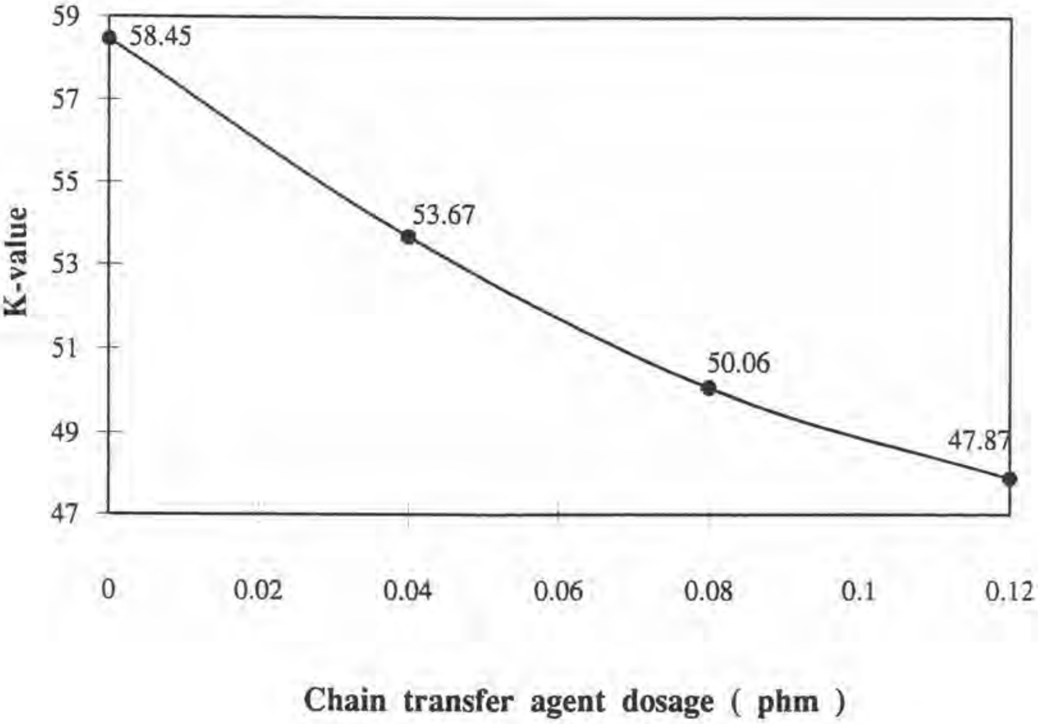

Figure 4.4 Relationship between chain transfer agent dosage and K-value at the polymerization temperature of 69°C

4.3 Effect of Polymerization Temperature on The Properties of Low Molecular Weight PVC Resin

The properties of PVC resin with K-value of 50 obtained from four polymerization temperature are shown in Table 4.1.

Table 4.1 Effect of polymerization temperature on resin properties

Properties	Polymerization temperature			
	81°C without CTA	77°C with 0.027phr CTA	73°C with 0.047phr CTA	69°C with 0.080phr CTA
Mean particle size (μm)	118	114	109	101
Distribution coefficient of particle size	0.394	0.370	0.322	0.311
Bulk density (gm/ml)	0.389	0.406	0.434	0.456
Cold plasticizer absorption (phr)	12.9	14.2	14.8	15.6
Fish eye (points)	349	92	22	26

The trend of each PVC properties is discussed as follows:

4.3.1 Mean Particle Size and Distribution Coefficient of Particle Size

In VCM suspension polymerization, the particle size and distribution coefficient of particle size of PVC resin depends on stirring speed and suspending agent. The VCM is dispersed into small droplets by mechanical stirring while the suspending agent stabilizes the VCM droplets and controls agglomeration of the interparticle and intraparticle of the PVC grains. The size and shape of PVC grains depend on the dispersing power of suspending agent. The suspending agent also has influence on bulk density and porosity of PVC resin.

In this study, the stirring speed and amount of suspending agent in each polymerization temperature were constant. It was found that when the polymerization temperature decreased, the particle size of PVC resin also decreased (Figure 4.5).

Figure 4.6 shows the relationship between distribution coefficient of particle size and polymerization temperature. The distribution coefficient of particle size was better at low temperature. The influence of suspending agent on the mean particle size and distribution coefficient of particle size was due to the partially hydrolyzed poly(vinyl acetate) which acted as the suspending agent. Poly(vinyl acetate) could easily precipitate at high polymerization temperature and hence the efficiency of suspending agent was lowered.

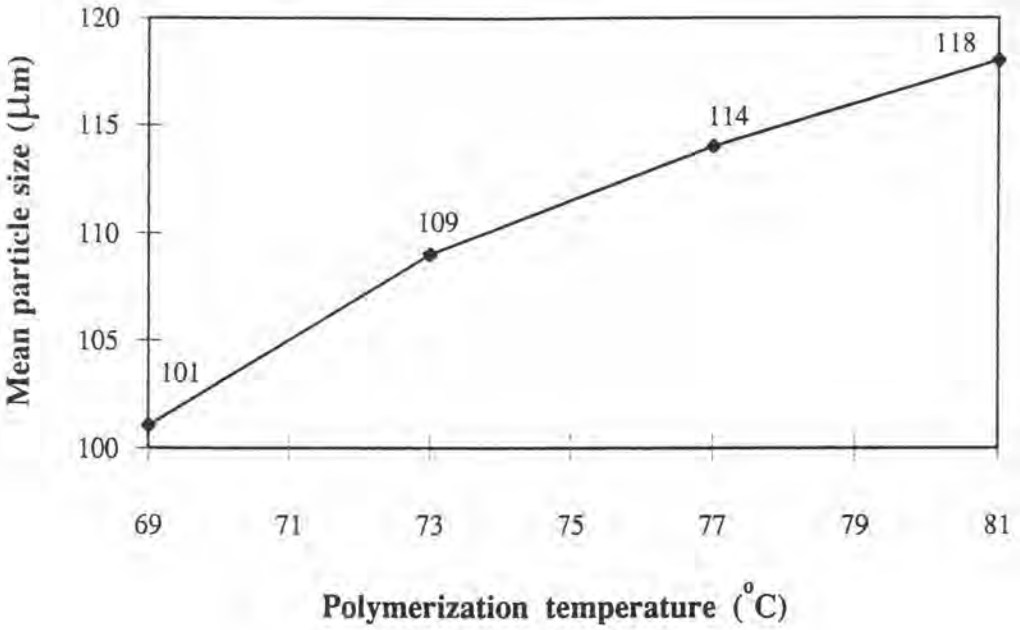

Figure 4.5 Relationship between particle size and polymerization temperature

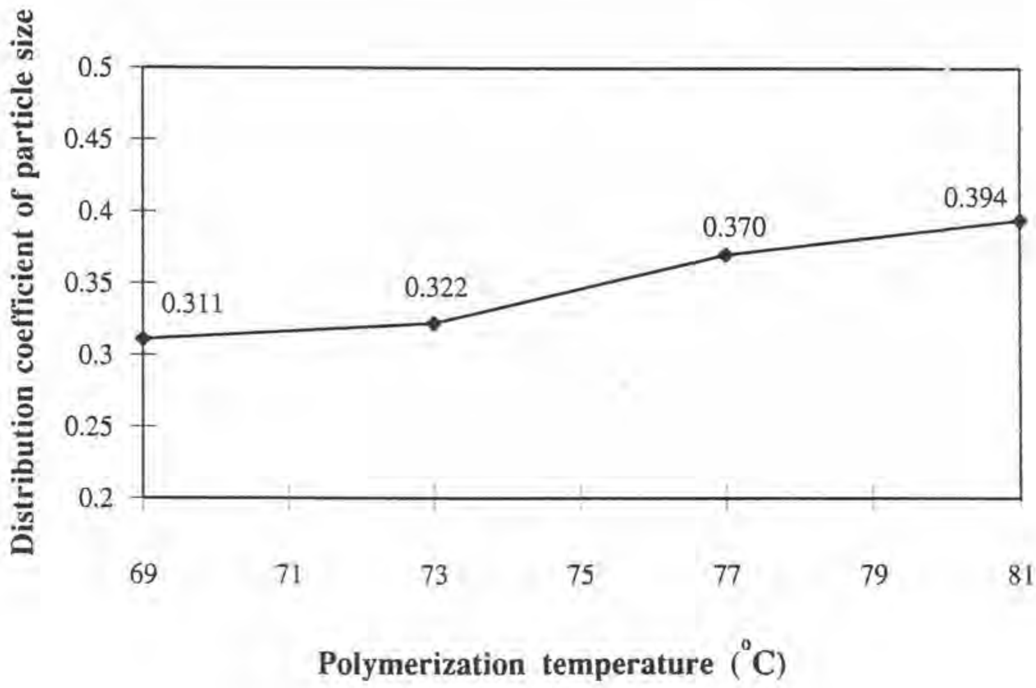

Figure 4.6 Relationship between distribution coefficient of particle size and polymerization temperature

4.3.2 Bulk density

Bulk density of PVC resin increases with low porosity and the wide scale of distribution of particle size since the void space are small. In addition, the shape also influences to bulk density.$^{(10)}$ In this study, it was found that the porosity of PVC resin decreased at higher polymerization temperature. However, the bulk density also decreased (Figure 4.7).

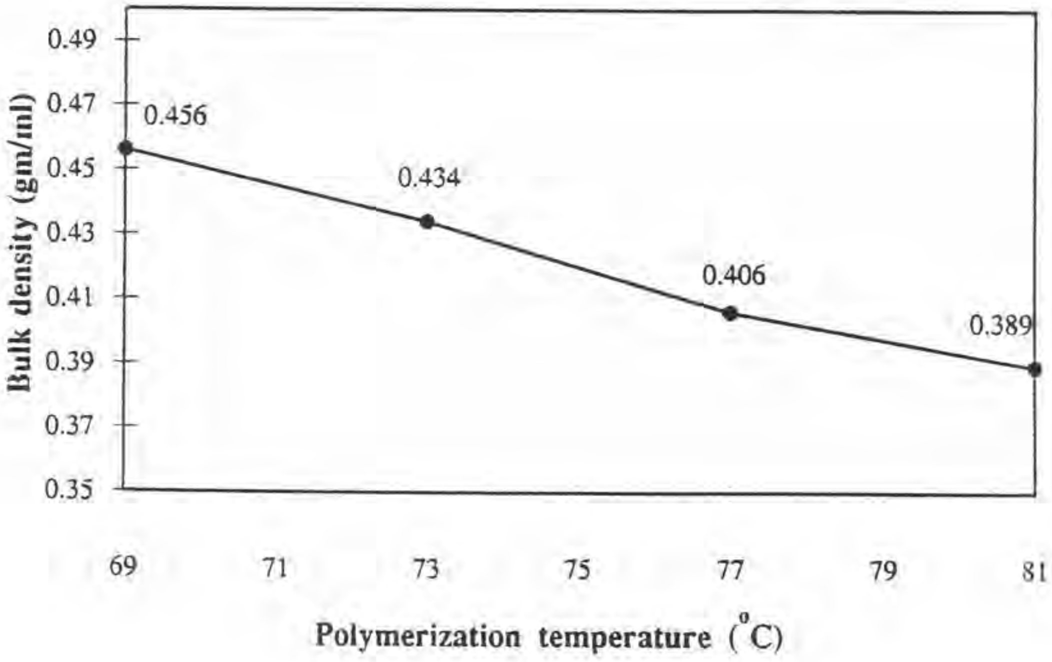

Figure 4.7 Relationship between bulk density and polymerization temperature

To explain these results, SEM of PVC resins obtained from differnt polymerization temperatures were taken (Figures 4.8 - 4.11). At higher temperature, the shape of PVC grains was irregular and therefore increased the void space of packing.

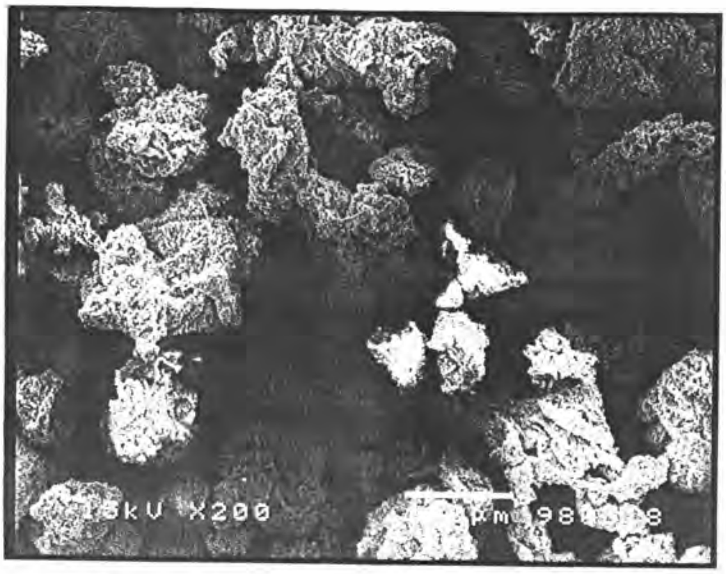

Figure 4.8 SEM of PVC grains prepared at the polymerization temperature of 81°C without chain transfer agent

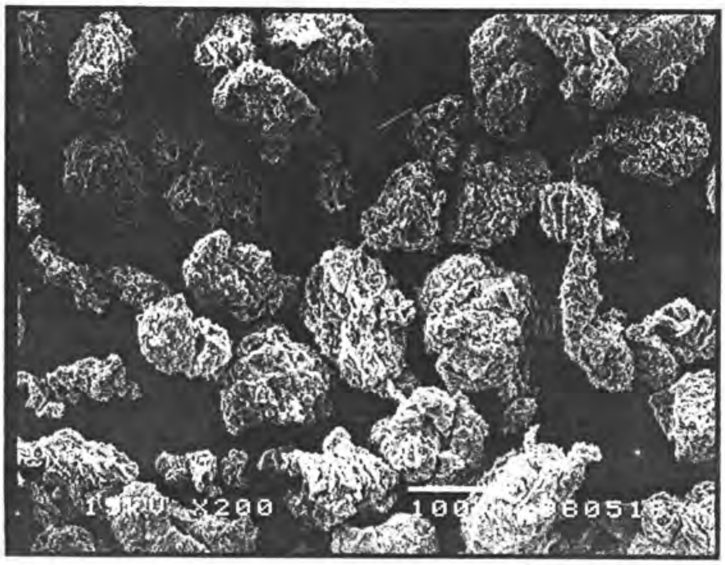

Figure 4.9 SEM of PVC grains prepared at the polymerization temperature of 77°C in the presence of 0.027 phm of chain transfer agent

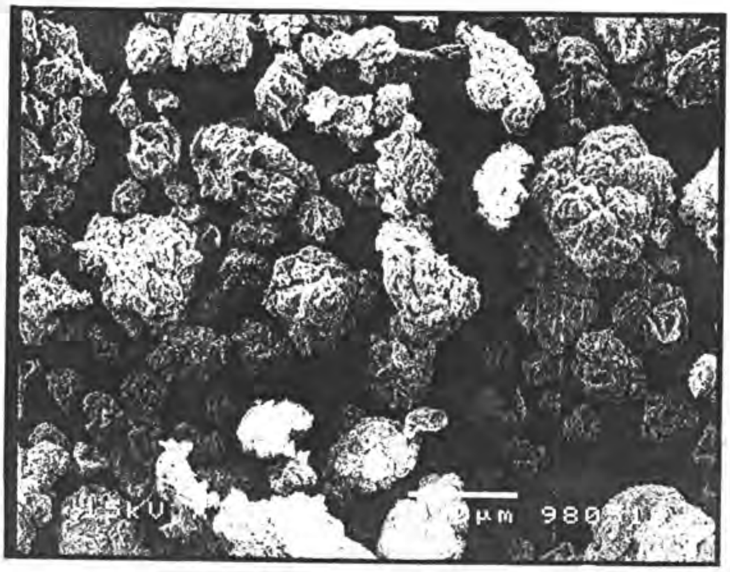

Figure 4.10 SEM of PVC grains prepared at polymerization temperature of 73°C in the presence of 0.047 phm of chain transfer agent

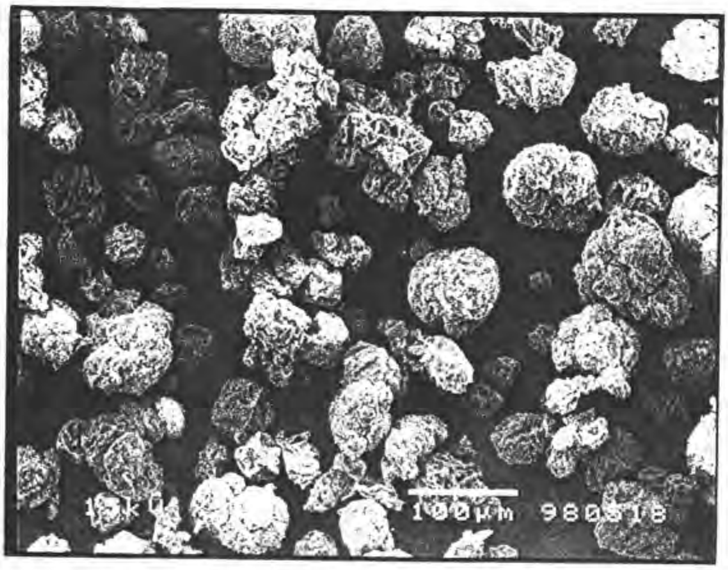

Figure 4.11 SEM of PVC grains prepared at polymerization temperature of 69°C in the presence of 0.080 phm of chain transfer agent

4.3.3 Cold plasticizer absorption (CPA)

CPA is the ability of PVC resin to absorb plasticizer. The important property influences CPA is the porosity of PVC grains. High porosity of PVC resin improves the CPA, which is good property of PVC resin. Since it can absorb large quantities of plasticizers, stabilizers, lubricants, fillers, pigments and remains a free flowing material on the compounding stages of processing in a short spend time. In rigid formulations, the presence of large quantities of external lubricant on the grain surface prolongs the gelation process which, if delayed to a point too far along the extruder profile, will have a damaging effect on machanical properties.(3) In addition, high porosity PVC grains reduces a number of fish eyes and also improves the VCM release property of the PVC particles. This allows residual VCM to be reduced to safe levels without causing degradation and discoloration during the VCM removal process.(11)

Figure 4.12 shows a relationship between cold plasticizer absorption and polymerization temperature. The porosity of PVC grains increased as the polymerization temperature decreased. The polymerization temperature is an important variable used in practice to control molecular weight but this also has a marked effect on grain porosity.(3) The growth of the primary particles at higher polymerization temperatures produces a very dense morphology. However, use of secondary suspending agent sush as PVA with low degree of hydrolysis can reduce this densification effect.(11) In addition, the agitation rate, type of initiator and water:VCM ratio also influence the porosity of PVC resin.

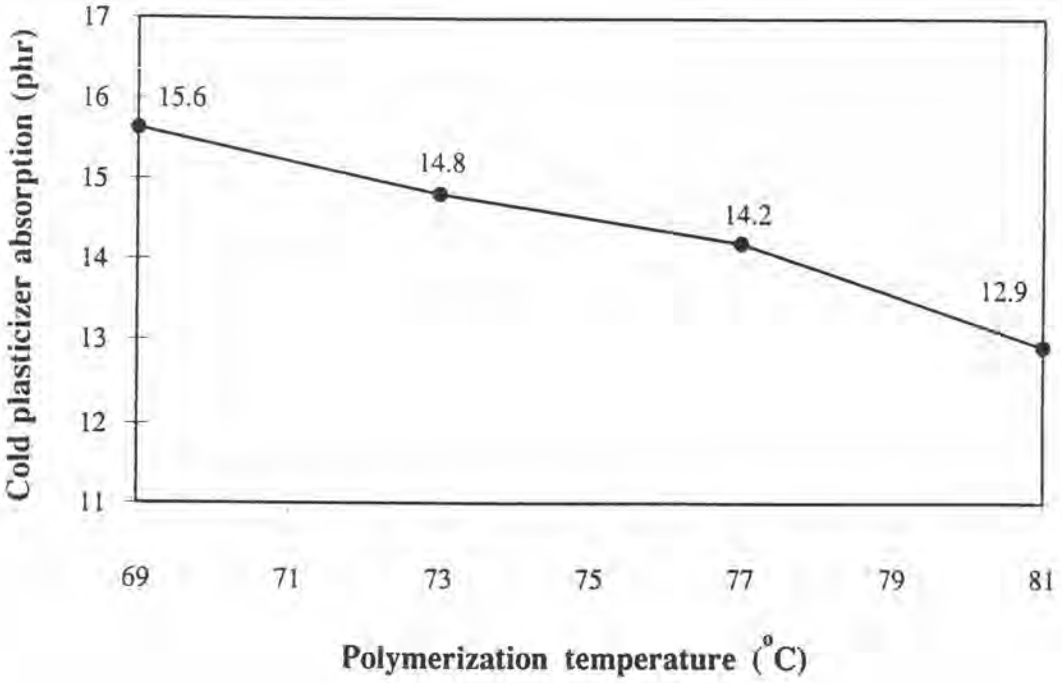

Figure 4.12 Relationship between cold plasticizer absorption and polymerization temperature

4.3.4 Fish eyes

Fish eyes are small globular mass which has not blended completely into the surrounding material and is particularly evident in a transparent or translucent material. In PVC, Fish eyes are hard specks of polymer which are not dispersed on processing and thus persist in the finished product.(11) They can originate during the polymer production, but may also be formed in melt processing as a consequence of non-uniform fusion. In opaque PVC materials, they appear as nids on the surface. Fish eyes in plasticized PVC usually occur from oversized and nonporous particles or dense morphology of PVC.

Figure 4.13 depicts a relationship between fish eyes and polymerization temperature. The PVC obtained from polymerization temperature of 81°C without chain transfer agent had large amount of fish eyes. Lower polymerization temperatures (77°C, 73°C and 69°C), reduced the amount of fish eyes. This is because low polymerization temperature increases cold plasticizer absorption or porosity of PVC grains which results in reduction of fish eyes .

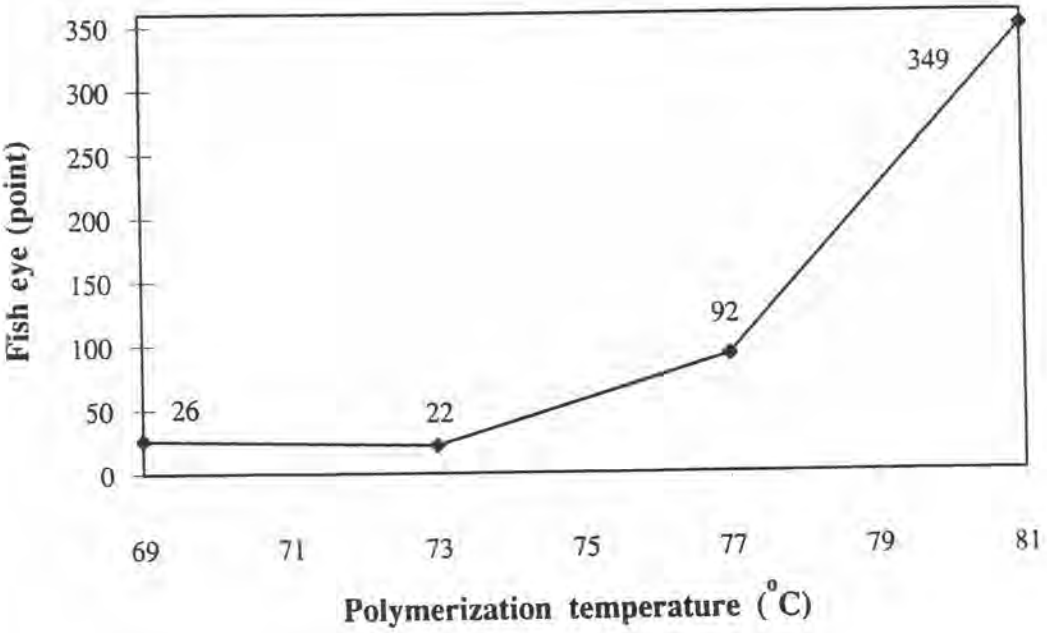

Figure 4.13 Relationship between fish eye and polymerization temperature

4.4 Properties of PVC Dry Blend

The properties of PVC dry blend with K-value of 50 obtained from four polymerization temperature are shown in Table 4.2.

Table 4.2 Effect of polymerization temperature on dry blend properties

Properties	Polymerization temperature			
	81°C without CTA	77°C with 0.027phr CTA	73°C with 0.047phr CTA	69°C with 0.080phr CTA
Fusion torque (Nm)	54.8	54.5	51.6	44.4
Dynamic heat stability (min)	19.3	20.3	19.2	19.2
Melt flow index (gm/10min)	30.8	30.0	30.0	28.8
Izod impact strength (kg-cm)/cm	1.52	0.63	1.41	0.66
Heat deflection temperature (°C)	72	72	72	72

The trend of each PVC dry blend properties is discussed as follows:

4.4.1 Fusion torque

Fusion torque is a torque which occurs at fusion point when all polymer particles are merged into a melt. The torque value at fusion point can be related to the power required for the fusion of a particular composition in a given production machine. The polymers with low torque at fusion point require lower energy for processing.

Figure 4.14 shows the relationship between fusion torque and polymerization temperature. The lowest fusion torque was obtained at 69°C. This is because the PVC grains obtained from this temperature had the highest porosity and hence required low energy for precessing.

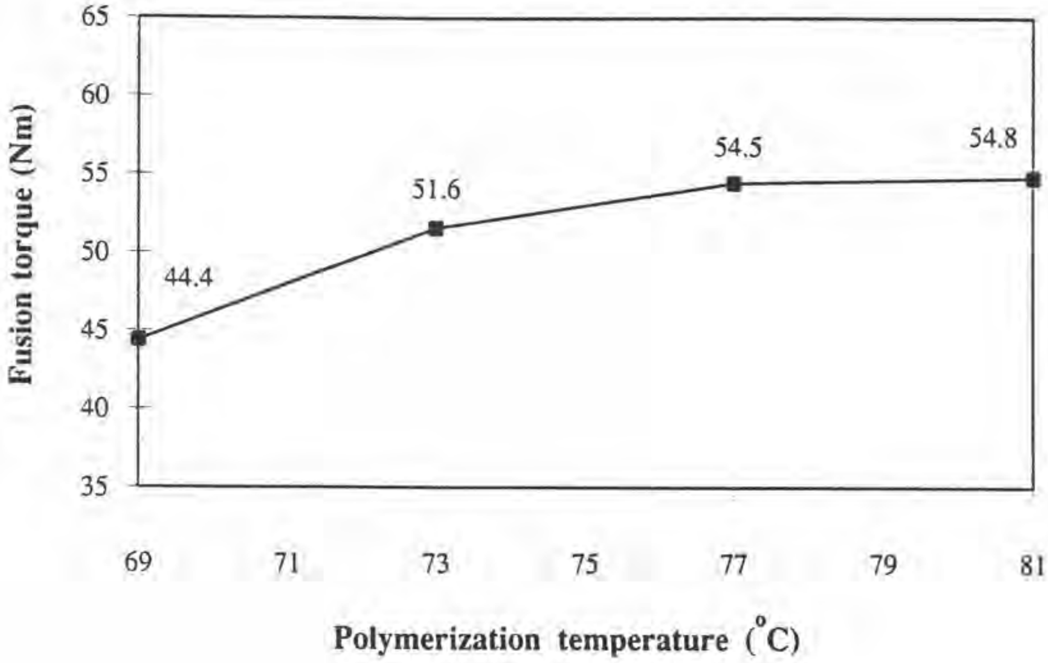

Figure 4.14 Relationship between fusion torque and polymerization temperature

4.4.2 Heat stability

4.4.2.1 Static heat stability testing (Figure 4.15)

4.4.2.2 Dynamic heat stability testing

(a) By use of continuous rolling at 180°C (Figure 4.16)

(b) By use of Brabender plasticorder (Figure 4.17)

Generally, use of chain transfer agent on the preparation of low molecular weight PVC can improve heat stability of PVC.(2,6) The disadvantage of chain transfer agent is the reduction of polymerization rate and therefore the amount of initiator was increased to control a constant polymerization time in each batch. Using high amount of initiator gave high initiator residue after polymerization which caused lower heat stability of PVC. Another factor which effects the heat stability is the temperature and time required for unreacted VCM removal. High temperature and long time result in the reduction of heat stability. Removal of reacted VCM could be done easily in PVC grains with high porosity.

From Figures 4.15 - 4.17, the PVC obtained from different temperatures exhibited with no significant difference heat stability.

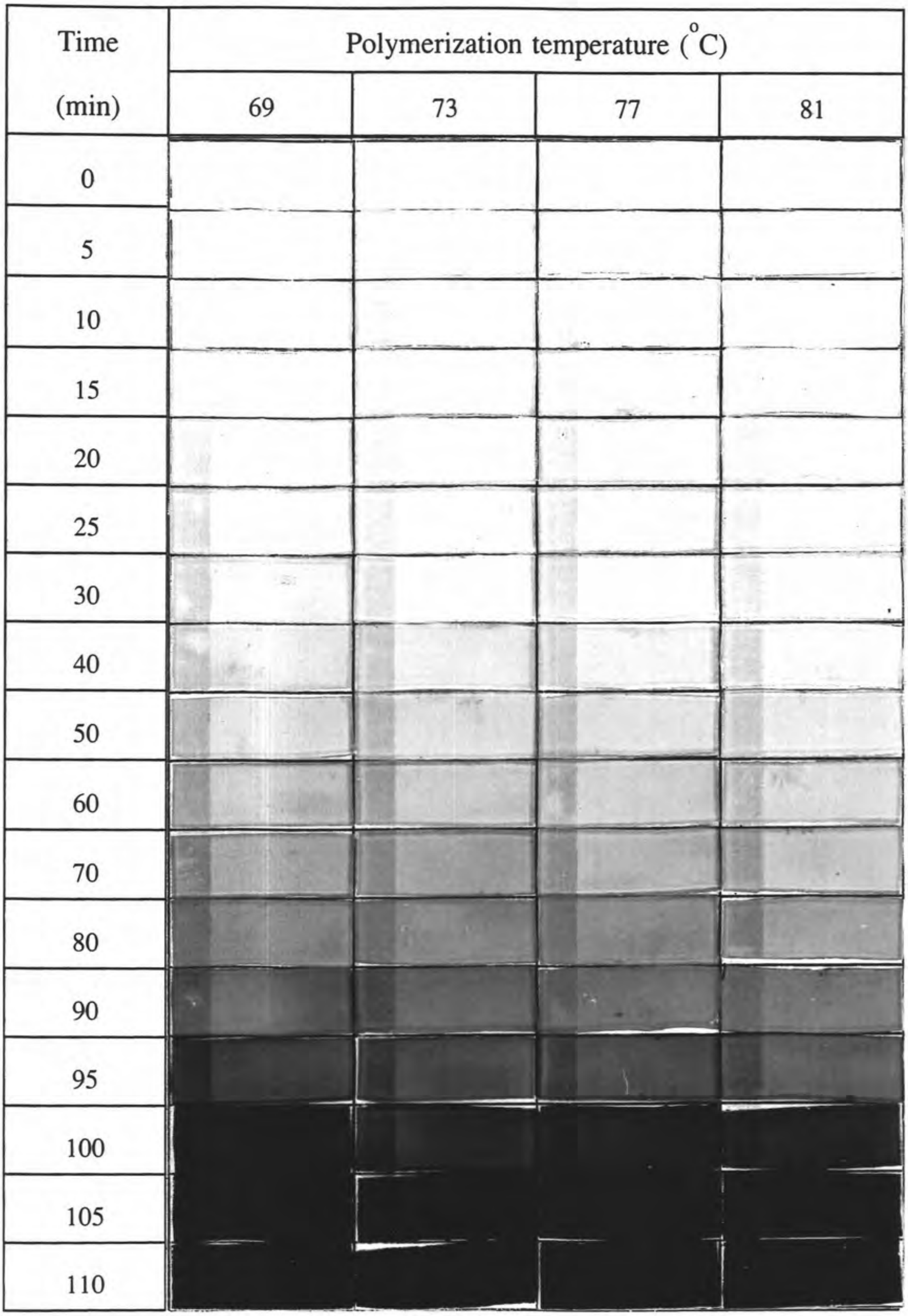

Figure 4.15 Static heat stability test at 180^{o}C

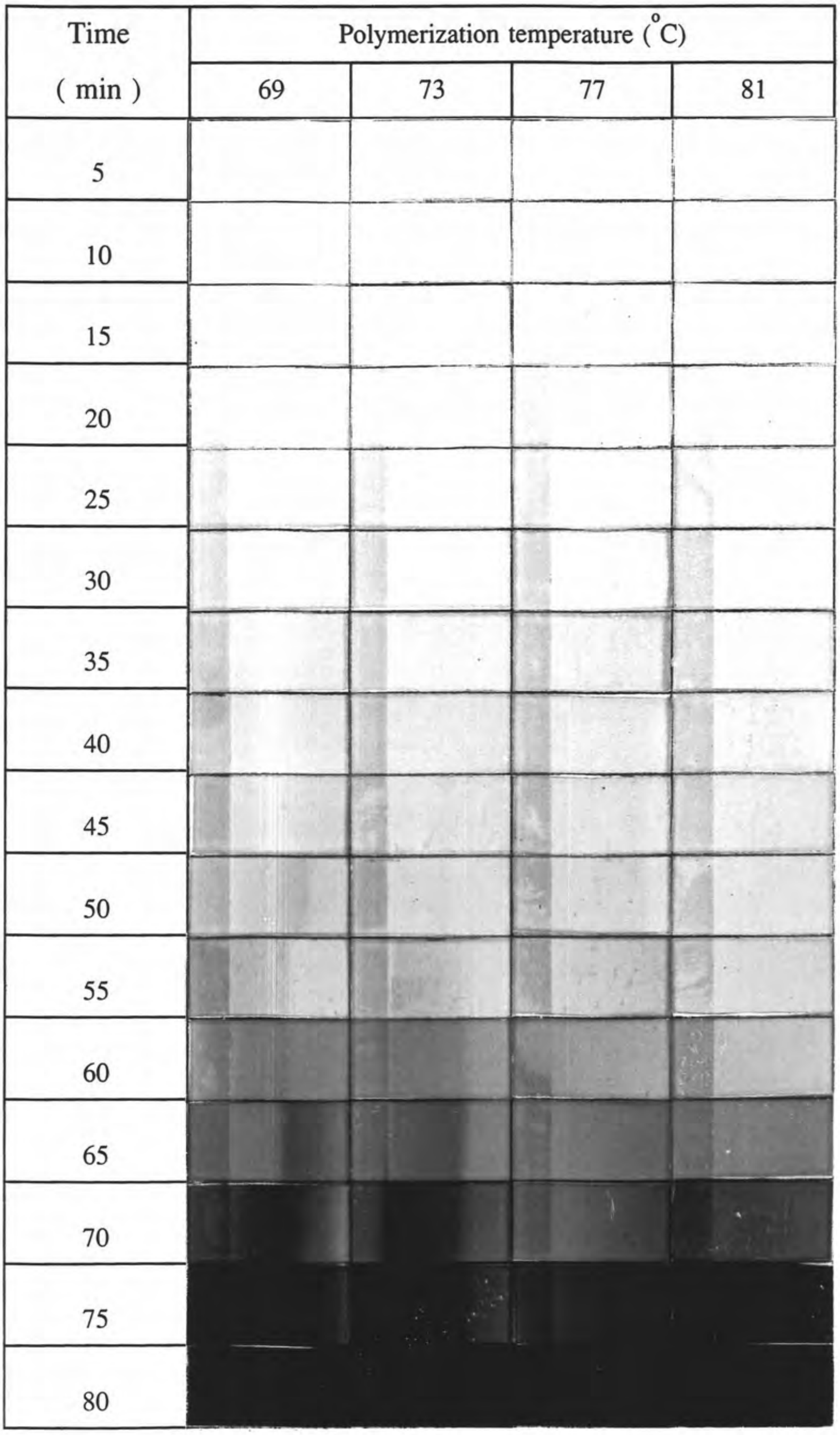

Figure 4.16 Continuous rolling test at 180°C

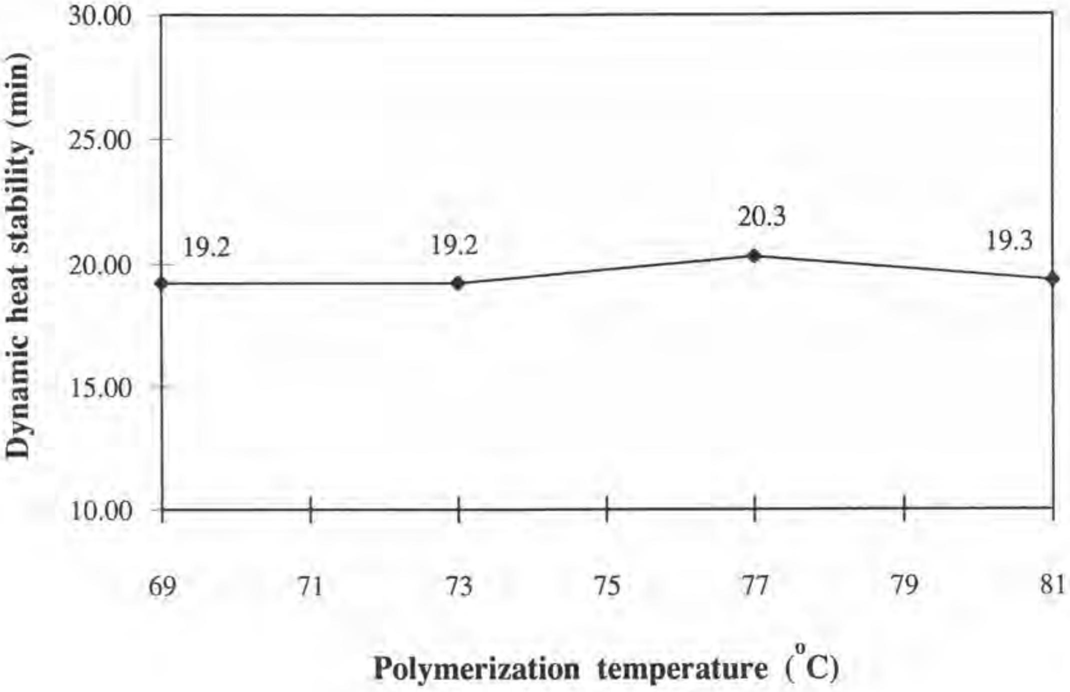

Figure 4.17 Relationship between dynamic heat stability and polymerization temperature

4.4.3 Melt flow index

Melt flow index depends on the molecular weight of PVC. A high molecular weight PVC is more resistant to flow than a low molecular weight PVC.(13)

Figure 4.18 shows a relationship between melt flow index and polymerization temperature. There are little change in melt flow index of each samples since all samples have the same K-value.

4.4.4 Izod impact strength

Figure 4.19 depicts a relationship between izod impact strength and polymerization temperature. The impact strength depends on degree of crystallinity and polymer molecular weight.(13,14) All PVC samples showed almost the same impact strength since they have the same molecular weight.

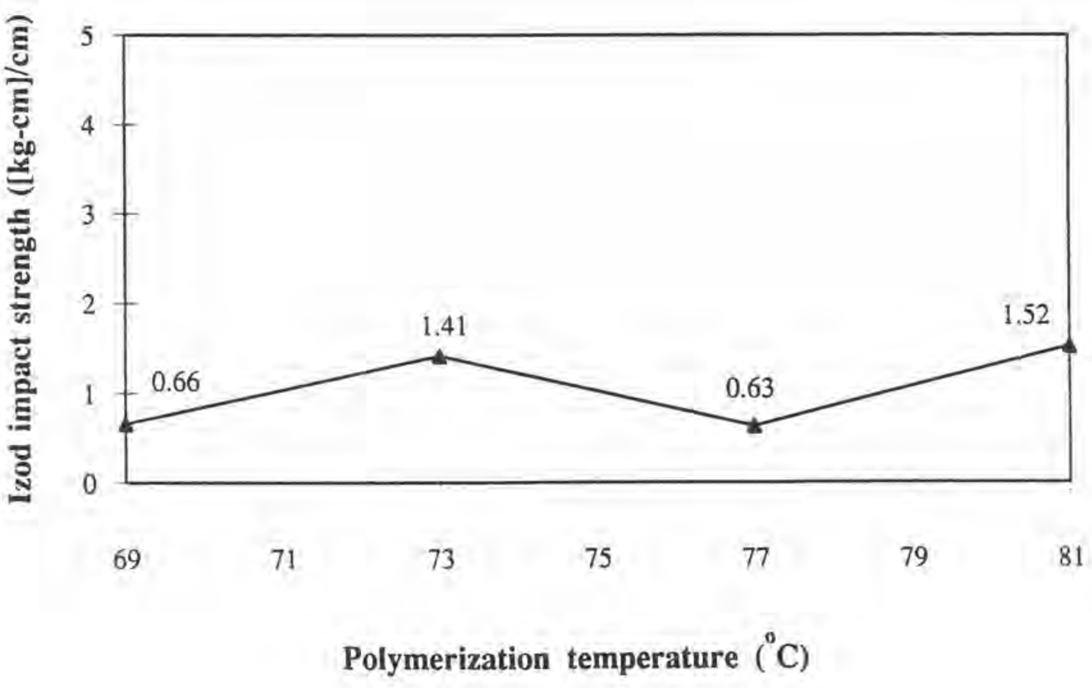

Figure 4.1? Relationship between izod impact strength and polymerization temperature

4.4.5 Heat deflection temperature (HDT)

The measurement of heat deflection temperature is one of various methods in determining the thermal properties of PVC. Heat deflection temperature is a single point measurement of short term heat resistance. The residual stress of the specimen, specimen thickness, specimen preparation, apply load of test and molecular weight of test PVC effect the heat deflection temperature.(13)

Figure 4.20 shows a relationship between heat deflection temperature and polymerization temperature. All PVC samples showed the same heat deflection temperature since they have the same molecular weight.

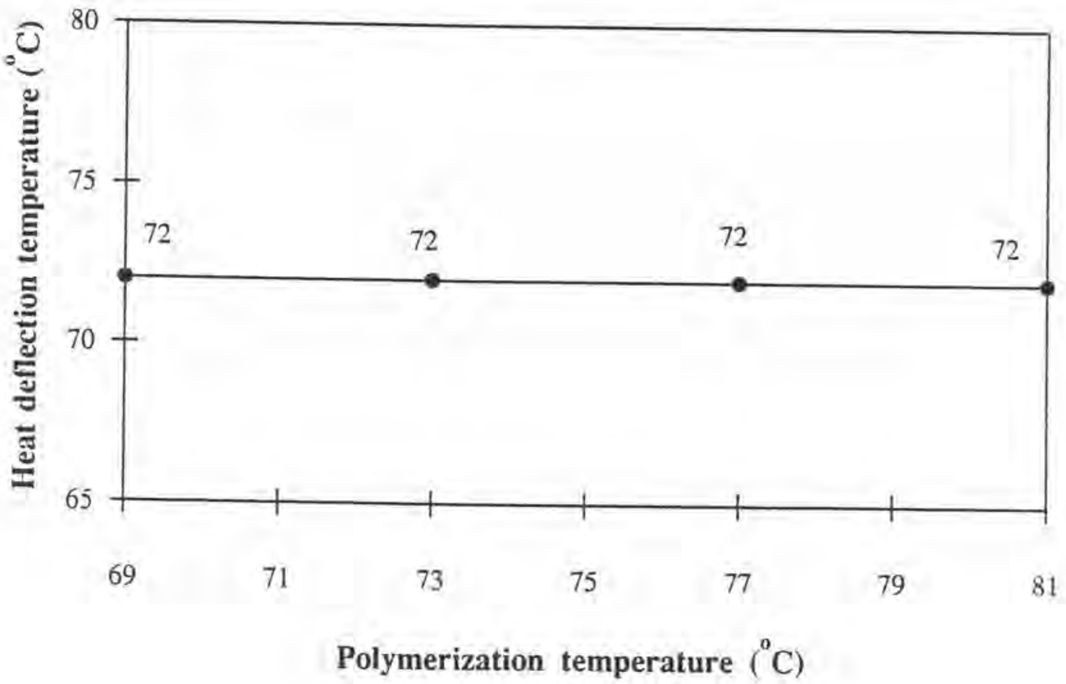

Figure 4.20 Relationship between heat deflection temperature and polymerization temperature