# CHAPTER II

# THEORY AND LITERATURE REVIEW

## 2.1 Suspension Polymerization of Vinyl Chloride Monomer

Suspension PVC is produced by dispersing the droplets of liquid vinyl chloride monomer (VCM), stabilized by a suspending agent, in water in an agitated reactor. The monomer contains dissolved initiator and when the contents of the reactor are heated, the initiator decomposes and starts the polymerization.[4] The polymerization of vinyl chloride is an exothermic reaction (-1540 KJ/Kg VCM). This heat is removed by cooling water in the autoclave jacket and/or autoclave condenser. The autoclave pressure will be steady at the autogenous pressure of VCM at the polymerization temperature until 75% conversion of VCM to PVC. The pressure then begins to fall. Suspension polymerization of VCM is usually stopped when 80-90% of the VCM is converted to PVC. The residual VCM is then removed from the suspension of PVC in water by a process termed stripping. The stripping slurry is dewatered using a centrifuge, the PVC resin is dried, resulting in a free flowing PVC powder. The outline of the VCM suspension polymerization process is shown diagrammatically in Figure 2.1.[3]

In VCM suspension polymerization, water is present to serve as a continuous phase and causes the VCM to be broken up into discrete droplets. Water also acts as a heat transfer medium and as a carrier for the protective

colloid. The VCM phase is broken up into 30-150 micron droplets by the comminuting action of the agitation and prevented from coalescing by action of protective colloid. A minimun quantity of water is required to fill all the spaces between the spherical VCM particles and to provide some free water to ensure a low viscosity mixture. The protective colloid acts by stabilizing the VCM droplet against coalescence in the early stages of polymerization and by controlling the aggregation step as shown in Figure 2.2. Therefore, a fine grain (50 micron) of controlled internal structure can be achieved. As polymerization proceeds, a certain amount of coalescence occurs, and yields the desired final grain size of about 100-150 micron and the desired grain porosity.[3]

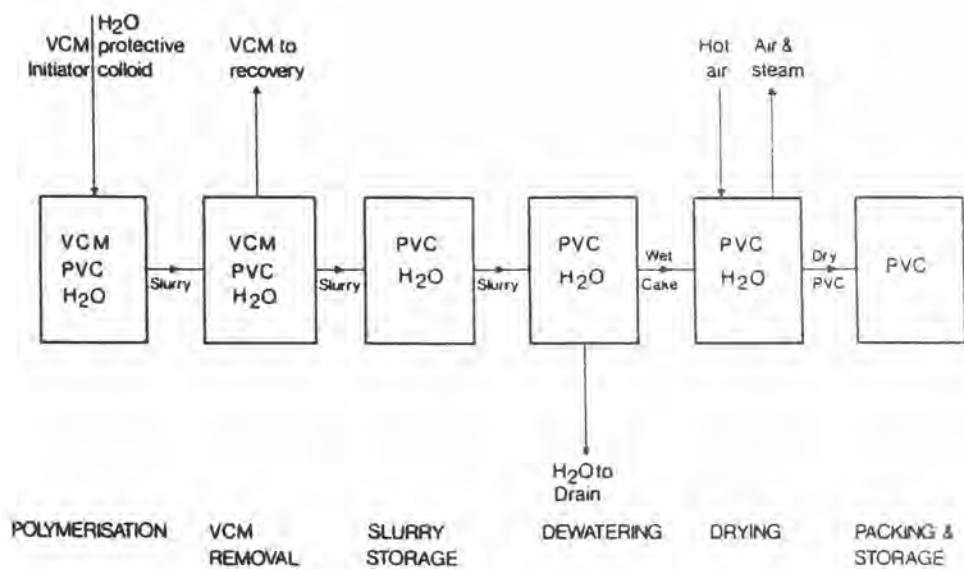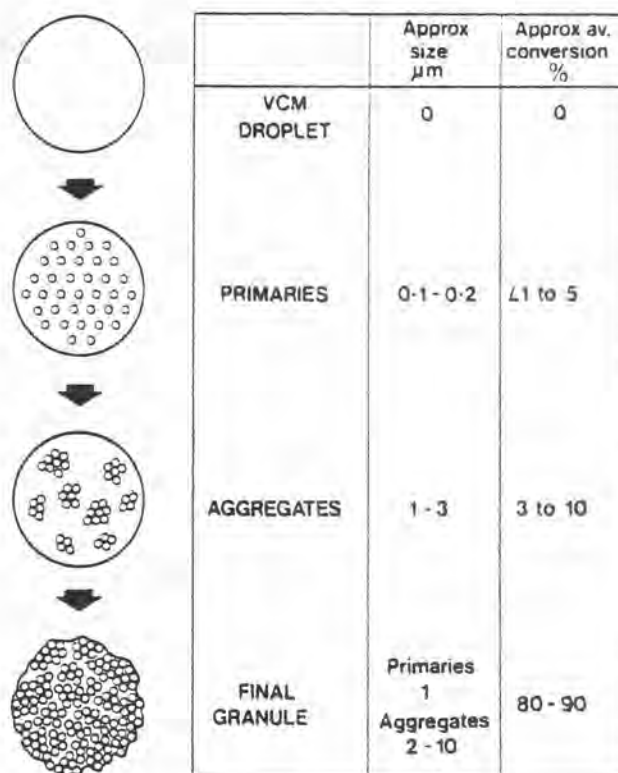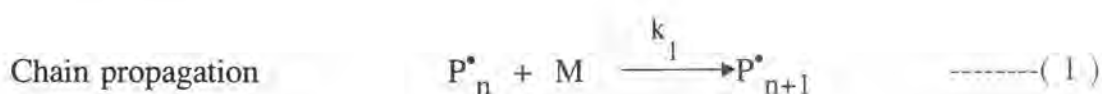Figure 2.1 The outline of the VCM suspension polymerization process.[3]

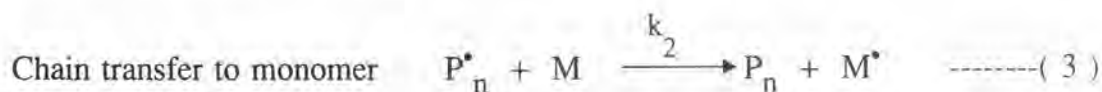| | Approx size µm | Approx av. conversion % |
|---|---|---|
| VCM DROPLET | 0 | 0 |
| PRIMARIES | 0·1 - 0·2 | ⊿1 to 5 |
| AGGREGATES | 1 - 3 | 3 to 10 |
| FINAL GRANULE | Primaries 1 Aggregates 2 - 10 | 80 - 90 |

Figure 2.2 VCM suspension polymerization-precipitation of PVC within droplets.[3]

## 2.2 Molecular Weight Control of VCM Polymerization

The vinyl chloride polymerization is growing via the free radical addition polymerization process. The molecular weight of the PVC does not depend on the conversion or on the initiator concentration but depends on polymerization temperature. This can be explained by considering the three processes that control the molecular weight of free radical polymerization : chain propagation, chain transfer of monomer and chain termination by disproportionation or by coupling. These processes may be represented as follows: [5]
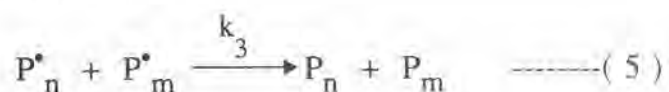
Chain propagation $\quad P^\bullet_n + M \xrightarrow{k_1} P^\bullet_{n+1}$ --------( 1 )

Rate of propagation, Rp $= k_1 [M][R^\bullet]$ --------( 2 )

Chain transfer to monomer $\quad P^\bullet_n + M \xrightarrow{k_2} P_n + M^\bullet$ --------( 3 )

$$M^\bullet + M \longrightarrow P^\bullet_2$$

Rate of chain transfer, $R_{tr} = k_2 [M][R^\bullet]$ --------( 4 )

Chain termination by disproportionation

$$P^\bullet_n + P^\bullet_m \xrightarrow{k_3} P_n + P_m \quad\text{--------( 5 )}$$

Chain termination by coupling

$$P^\bullet_n + P^\bullet_m \xrightarrow{k_4} P_{n+m} \quad\text{--------( 6 )}$$
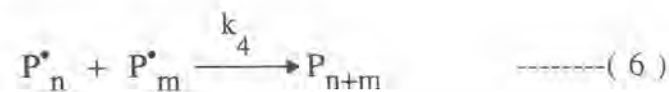
Rate of termination, $R_t \quad = \quad k_3 [R^\bullet]^2 + k_4 [R^\bullet]^2$ --------( 7 )

$$= \quad k_5 [R^\bullet]^2 \qquad \text{--------( 8 )}$$

Where

$P_n^\bullet \quad = \quad$ Polymer radical of length $n$ unit

$P_n \quad = \quad$ Polymer of length $n$ unit

$M \quad = \quad$ Monomer

$M^\bullet \quad = \quad$ Monomer radical

$[R^\bullet] \quad = \quad$ Concentration of free radical

$[M] \quad = \quad$ Concentration of monomer

In the case of PVC, $k_5 [R^\bullet]^2$ is small and gets large enough to become important only if an unusually high level of initiator is used in order to increase $[R^\bullet]$.[5] For normal initiator levels and polymerization rates, only chain transfer and propagation need to be considered. The molecular weight is then dependent on the relative rates of these processes :

The average degree of polymerization (DP) $\quad = \quad \dfrac{\text{rate of propagation}}{\text{rate of chain transfer}}$ ------( 9 )

$$= \quad \frac{k_1 [M][R^\bullet]}{k_2 [M][R^\bullet]}$$

$$= \quad \frac{k_1}{k_2}$$

The $k_1/k_2$ is related to polymerization temperature by Arrhenius equation relation :

$$k = A_{exp} (-E/RT) \qquad \text{---------( 10 )}$$

where

$$A = \text{constant}$$
$$E = \text{activation energy}$$
$$R = \text{universal gas constant}$$
$$T = \text{absolute temperature}$$

From Arrhenius equation, $k_1$ and $k_2$ are function of temperature and thus the molecular weight depends on polymerization temperature. The molecular weight of PVC increases with decreasing polymerization temperature, while the molecular weight decreases with increasing polymerization temperature.

The molecular weight is usually obtained from the relative viscosity of dilute polymer solution compared with pure solvent, the results being expressed as ISO Viscosity Numbers from which "K-values" can be derived. The K-value for commercial PVC is usually in the range of 55-72 . The production of PVC with these K-value requires polymerization temperature between 50-72$^{o}$C. High temperatures produces low K-values. The relationship between polymerization temperature and K-value and molecular weight of PVC are shown in Figures 2.3 and 2.4, respectively.
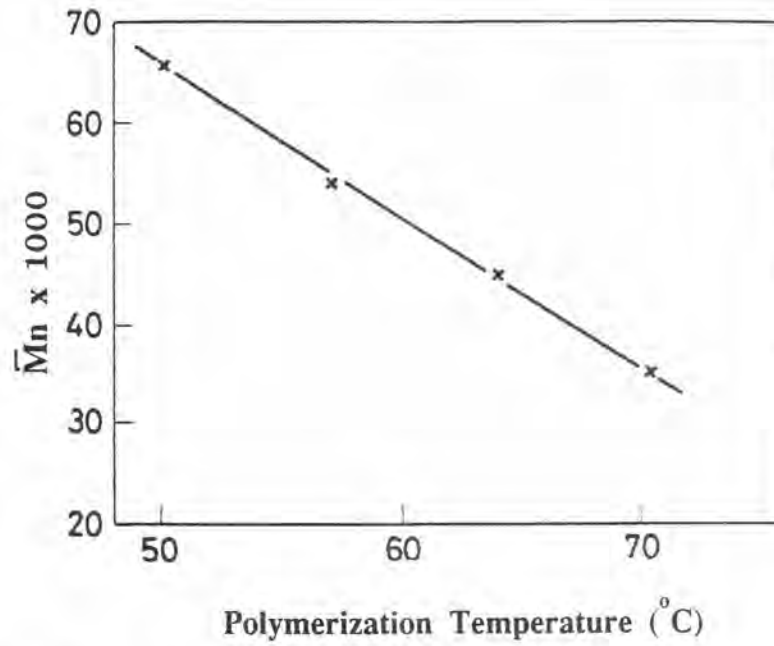
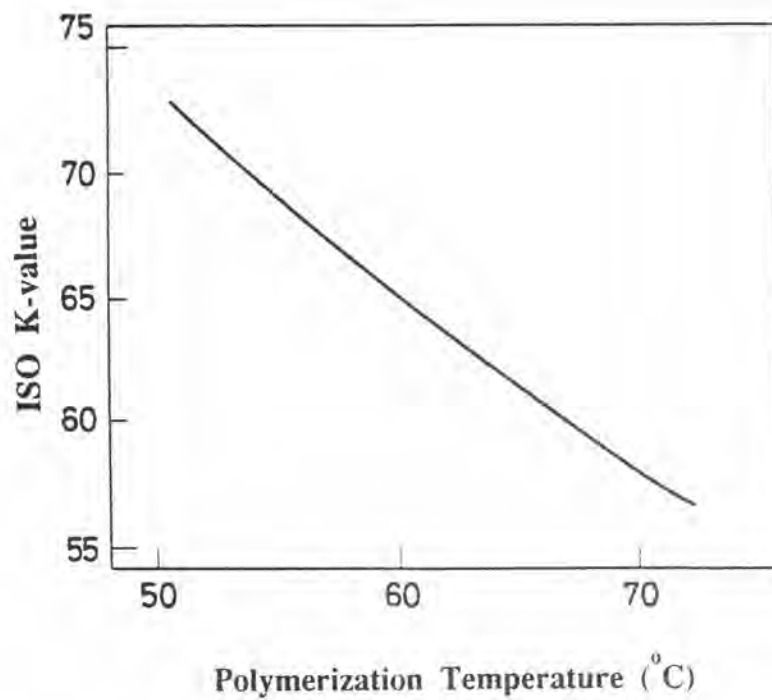Figure 2.3 The effect of polymerization temperature on molecular weight of PVC.[3]



Figure 2.4 The effect of polymerization temperature on K-value of PVC.[3]

## 2.3 Preparation of Low Molecular Weight PVC by Using High Temperature

This is a normal method for polymerizaion of PVC to obtain low molecular weight PVC, such as the K-value of 50 requires polymerization temperature at about $80^{\circ}C$ and polymerization pressure at about 15 kg/cm$^2$. These conditions are difficult to control and careful operation is needed. A table of polymerization pressure at different temperature is given in Appendix page 59. High polymerization temperature produces a very dense PVC grain (Figure 2.5) which makes the removal of unreacted VCM from the polymer during stripping difficult. Use of higher temperature to remove unreacted VCM consumes energy and influences color and heat stability of PVC resin.
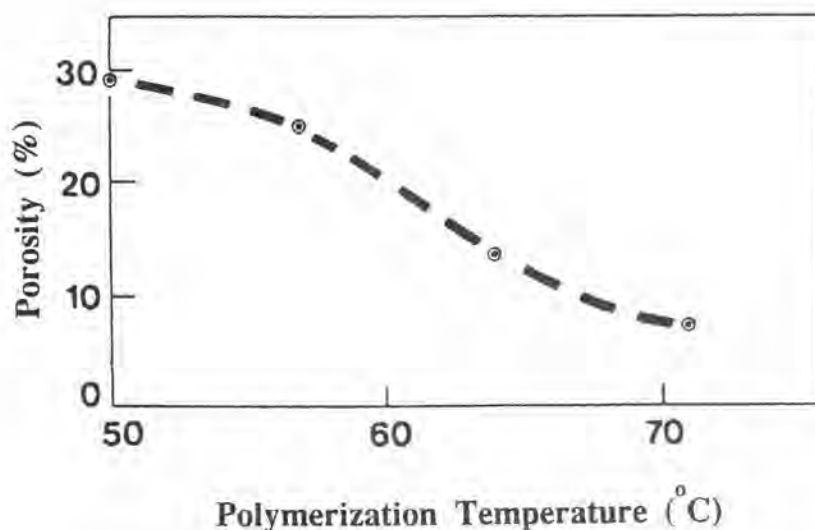


Figure 2.5 Variation of porosity (cold plasticizer absorption) with polymerization temperature. [3]

## 2.4 Preparation of Low Molecular Weight PVC by Addition of a Chain Transfer Agent (CTA)

Low molecular weight PVC can also be produced at lower temperature by an addition of chain transfer agent to the polymerization mixture. CTA are saturated hydrocarbons such as n-pentane and n-hexane ; saturated or unsaturated chlorinated hydrocarbons such as carbon tetrachloride and trichloroethylene; aldehydes such as propionaldehyde; and certain mercapto-containing organic compounds such as dodecyl mercaptan. Typical mercapto-containing CTA is very popular due to high activity.[6]

The phenomenon of molecular weight reduction in radical polymerization might be explained by free radical mechanism in which the reaction were as follows:

$$R(M)_n^{\bullet} + SX \longrightarrow R(M)_nX + S^{\bullet} \qquad \text{--------(11)}$$

$$S^{\bullet} + M \longrightarrow M^{\bullet} \qquad \text{--------(12)}$$
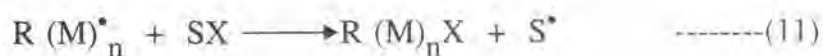
where

$M$     =    vinyl monomer

$SX$    =    chain transfer agent

$X$     =    radical extractable group

$R(M)_n^{\bullet}$ = growing polymer radical

From the above reaction, the product of the reaction is a dead polymer and a new radical, and therefore the chain transfer agent can control the molecular weight of polymer. If the new radical is active enough, a new chain is initiated by the addition of more monomer. If the rate of addition of

monomer to the new radical is rapid enough, no change in the overall rate of polymerization will be observed. In general, the addition of chain transfer agents tends to reduce the rate of polymerization. Small amount of chain transfer agent with high activity is needed in the polymerization. [7]

## 2.5 Relevant Literature Review

Kuwata, Ogawa and Kurimoto [6] studied the method for preparing PVC or copolymers having a relatively low molecular weight by using an organic compound containing a mercapto group and a hydroxy or carboxyl group in a molecule as a chain transfer agent. Due to their very high activity, these chain transfer agents are used in small amounts. The obtained polymers exhibited good physical properties.

Yamamoto, Maehara, Mitani, and Mizutani [2] prepared low molecular weight poly(vinyl chloride) with relatively low molecular weight (LMW-PVC) by suspension polymerization in the presence of chain transfer agents, such as mercapto compounds. The resultant LMW-PVC had good thermal stability. The degree of dehydrochlorination of the LMW-PVC obtained by using n-dodecylmercaptan increased with increasing the content of chain transfer agent. It was found that the LMW-PVC obtained by using mercapto compounds showed better thermal stability (discoloration property) than the one obtained without using these agents, at the same weight-average polymerization degree.

This research group also studied the blending effect of poly(vinyl chloride) with relatively higher molecular weight PVC (HMW-PVC) and relatively lower molecular weight PVC (LMW-PVC) by measuring thermal

stability and fusion times. The thermal stability and fusion time of the blended PVC were improved when the small amount of LMW-PVC obtained by using mercapto compounds as a chain transfer agent is blended into HMW-PVC. At the LMW-PVC content in the range of 5-30 wt%, the thermal stability of the blended PVC showed significant improvement.