2

PVC MANUFACTURE TECHNOLOGY

2.1 MONOMER

Vinyl chloride is the sole monomer used in the production of PVC. Its structure and properties are given in Table 2.1.

Table 2.1. Typical properties of vinyl chloride

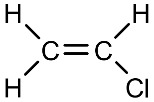
Property	Description
General	Vinyl chloride is a flammable, colorless gas with a sweet odor at room temperature. It is mainly used for production of PVC but also as a refrigerant and comonomer
Chemical structure	
Chemical formula	C_2H_3Cl
IUPAC name	1-chloroethene
Alternate names	chloroethylene, chloroethene, ethylene monochloride
Identifiers	CAS # – 75-01-4; EINECS – 200–831–0; UN # – 1086; RTECS – KU9625000
Molecular weight, g/mol	62.5
Odor	mild, sweet
Color	colorless
Melting point, °C	-153.8
Boiling point, °C	-13.37
Decomposition temperature, °C	450
Flash point, °C	-78
Autoignition temperature, °C	472
Explosive limits in air, vol%	3.6 and 33
Density, kg/m^3	2.56 (gas); 908.41 (liquid)
Vapor density (air=1)	2.15
Vapor pressure at 25°C, mm Hg	2600

Table 2.1. Typical properties of vinyl chloride

Property	Description
Solubility in water, wt%	0.95
Solubility of water in 100 g VC, ml	0.08 (20°C)
Solubility in solvents	alcohol, ether, carbon tetrachloride, benzene
Henry's law constant, atm m^3/mol	2.71E-02
Critical temperature, °K	432
Critical pressure, MPa	5.67
Enthalpy of vaporization, kJ/mol	21.998-23.3
Enthalpy of fusion, kJ/mol	4.92
Enthalpy of formation, kJ/mol	28.45
Specific heat capacity, J/kg/g	0.8592 (gas), 0.9504 (solid)
Heat capacity of liquid at 298.15K, J/molK	0.053625
Latent heat of vaporization, kJ/kg	333
Antoine equation parameters	A – 3.98598, B – 892.757, C – -35.051 (165.2-259.3K)
Octanol/water partition, $\log K_{ow}$	1.36
Odor threshold, ppm	3000
Half-life in air, h	few

2.2 BASIC STEPS OF RADICAL POLYMERIZATION

2.2.1 INITIATION

Vinyl chloride has low reactivity but its radical is highly reactive. For this reason, PVC is manufactured by radical polymerization. Initiation is a two step process, as given by the following reactions:

$$I \longrightarrow 2\dot{I} \quad \text{(I - initiator)}$$

$$\dot{I} + M \longrightarrow R^{\bullet} \quad \text{(M - monomer; } \dot{R} \text{ - growing polymer radical)}$$

First, the initiator produces free radicals which then react with monomer, forming a radical ready for the next step – propagation.

This method of initiation causes the chain end structure of PVC macromolecules to consist of initiator fragments.

Initiators are important components of industrial polymerization formulations. Table 2.2 shows chemical structures of the most common representatives with their half-life temperatures, HLT.

Table 2.2. Examples of common initiators[1,2]

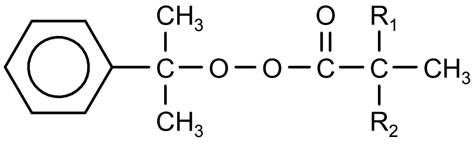
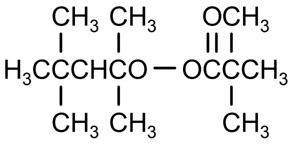
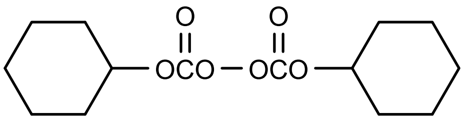
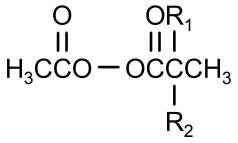
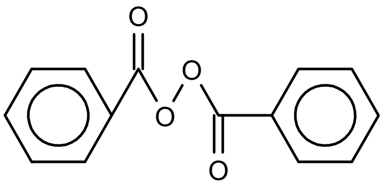
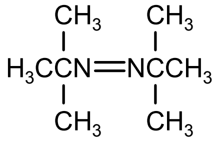
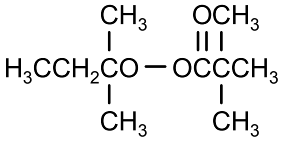
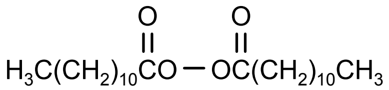
Name	Abr.	HLT, °C	Chemical formula
Cumyl peroxyneodecanoate	CUPND	55	
tert-Octyl peroxyneodecanoate	TOPND	56	 $H_3C\overset{CH_3}{\underset{CH_3}{C}}CH\overset{CH_3}{\underset{CH_3}{C}}O-O\overset{O}{C}\overset{CH_3}{\underset{CH_3}{C}}CH_3$
Dicyclohexyl peroxydicarbonate	CHPC	57	
tert-Butyl peroxyneodecanoate	TBPND	64	 $H_3C\overset{O}{C}O-O\overset{O}{C}\overset{R_1}{\underset{R_2}{C}}CH_3$
Benzoyl peroxide	BPO	65	

Table 2.2. Examples of common initiators[1,2]

Name	Abr.	HLT, °C	Chemical formula
2,2'-azobisbutylnitrile	AIBN	73	 $H_3C\overset{CH_3}{\underset{CH_3}{C}}N{=}N\overset{CH_3}{\underset{CH_3}{C}}CH_3$
tert-Amyl peroxypivalate	TAPPI	74	 $H_3CCH_2\overset{CH_3}{\underset{CH_3}{C}}O-O\overset{O}{\overset{\parallel}{C}}\overset{CH_3}{\underset{CH_3}{C}}CH_3$
Dilauroyl peroxide	LP	80	 $H_3C(CH_2)_{10}\overset{O}{\overset{\parallel}{C}}O-O\overset{O}{\overset{\parallel}{C}}(CH_2)_{10}CH_3$

Selection of initiator influences the molecular weight of polymer and the polymerization rate. The molecular weight is controlled by chain transfer to monomer and propagation rate. If the temperature of polymerization increases, the rate of chain transfer to monomer will be higher than the propagation rate. The higher the temperature, the lower the molecular weight. For PVC resins having K=70 and above, the polymerization temperature should be below 52°C. Initiators having HLT about 57°C are used as primary initiators. To boost the slow initial rate, initiators having HLT lower than 57°C are used. Less active initiators (TAPPI to LP) are used as secondary initiators in production of PVC grades below K=60.

2.2.2 PROPAGATION

The propagation reaction can be schematically written as

$$R^{\bullet} + M \longrightarrow R^{\bullet}$$

Addition of monomer increases molecular weight of the growing radical, which continues to react according to the same scheme. Vinyl chloride may add onto the polymer chain in two ways: head-to-head and head-to-tail. The head-to-tail addition prevails. But in some cases head-to-head structures are formed which contribute to the defect formation similar to any other anomaly of polymerization reaction, which result in other typical chain defects as discussed in Chapter 1.

From the point of view of polymerization conditions, defects are formed with increased incidence at high monomer conversions (above 60%).

Polymerization rate is almost independent of initiator concentration because the presence of polymer in the reaction mixture exerts a catalytic effect, promoting further polymerization. The catalytic effect of polymer is proportional to its actual surface area. The propagation rate constant, k_p, is given by the following equation:[1]

$$k_p = 3.3 \times 10^6 \exp\left\{-\frac{3700}{RT}\right\} \tag{2.1}$$

where:

R gas constant
T absolute temperature.

This equation confirms the previous statement that initiator concentration does not enter the relationship, which is only controlled by temperature.

The rate of polymerization is not uniform throughout the mixture because it is higher inside a swollen particle of polymer. This is most likely due to the catalytic effect of polymer and reduction of radical termination rate because of reduced mobility of the growing radical. The rate of polymerization is thus auto-accelerating, which, in combination with its high exothermic effect (106 kJ/mol), puts emphasis on effective cooling which controls the process rate and quality of the product.

2.2.3 TERMINATION

Termination occurs by disproportionation and combination, as shown by the following reactions:

$$R_1CH_2\dot{C}HCl + R_2CH_2\dot{C}HCl \longrightarrow R_1CH{=}CHCl + R_2CH_2CH_2Cl$$

$$R_1CH_2\dot{C}HCl + R_2CH_2\dot{C}HCl \longrightarrow R_1CH_2CHClCHClCH_2R_2$$

The rate constant of termination, k_t, is expressed by the following relationship:

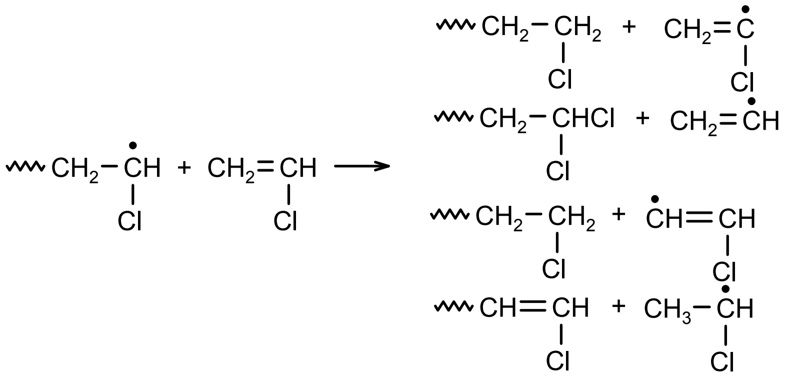
$$k_t = 1.3 \times 10^{12} \exp\left\{-\frac{4200}{RT}\right\}$$

The ratio of disproportionation to combination is difficult to determine but the combination is known to be a prevalent mechanism of termination.[1,5]

One peculiarity of PVC polymerization is that polymer is not soluble in its monomer and it precipitates when formed. Monomer is capable of swelling polymer, which results in a porous structure of polymer grains formed, as well as the possibility that reaction of polymerization continues in a portion of monomer used for swelling the already formed grains. This gives PVC peculiar morphological structures which can be manipulated by process.

2.2.4 CHAIN TRANSFER TO MONOMER

A growing radical may react with monomer, forming polymer and a monomer radical, which further grows, due to reaction with monomer. These reactions, called chain transfer reactions, may occur according to one of the schemes below:[1]



The third reaction scheme is considered to be the main reaction of a new radical generation based on activation energies of reactions.[1]

Chain transfer constant for PVC is given by the following equation:

$$C_m = 125\exp\left\{-\frac{7300}{RT}\right\} \qquad [2.2]$$

The values of C_m are large due to the high reactivity of vinyl chloride. This reaction controls the molecular weight of polymer. With temperature of reaction increasing, the value of constant increases, which results in an increased number of chain transfers and lower molecular weight of the resultant polymer.

Chain transfer to polymer results in formation of long branches as discussed in Chapter 1.[3]

Various chain transfer agents, such as dodecylmercaptan, 2-mercaptoethanol, α-thioglycerol, or thioglycolic acid, may be used to decrease molecular weight of the resultant polymer.[4]

2.3 POLYMERIZATION TECHNOLOGY

PVC production has grown by about 4% per year since 1990. The largest growth is experienced in Asia (especially in China), followed by North America and Europe.[6] There are four major methods of production of PVC, including bulk, emulsion, solution, and suspension polymerizations. Suspension polymerization is the most common since it accounts for 80% of world production of PVC (75% in USA and 93% in Japan).[6] It is followed by production of paste-type resins by emulsion (12% in the world) and microsuspension polymerization (3% USA and 5% Japan). Bulk polymerization contributes 8% of world production of PVC. Solution polymerization is not a commercial scale method.

2.3.1 SUSPENSION

Suspension polymerization is a batch process which includes four unitary operations:

- polymerization
- stripping residual vinyl chloride
- centrifugation of water suspension to remove water
- drying.

The typical formulation of reactor charge is given in Table 2.3.

Table 2.3. Typical formulation for suspension polymerization.[6]

Component	Concentration, parts
Vinyl chloride	100
Demineralized water	120
Suspending agent	0.05-0.1
Initiator	0.03-0.16

Types of initiators used are presented in Table 2.2 and their role is discussed in the previous section. A suspending agent (frequently called a protective colloid) prevents agglomeration of vinyl chloride droplets changing later into sticky particles of formed polymer. Without a suspending agent, uniformity of suspension will suffer and particle size will have a very broad range, with large lumps which will diminish the quality of PVC. Water soluble natural and synthetic polymers are known to prevent coalescence of droplets and agglomeration of particles. Partially hydrolyzed polyvinyl acetate (polyvinyl alcohol) and hydroxypropyl methylcellulose are the most popular suspension agents. Two types of commercial products are used: primaries and secondaries.[6] Primaries, which have a degree of hydrolysis in the range of 71 to 82%, are used to control particle size of PVC. Secondaries, which have a degree of hydrolysis in the range from 45 to 57%, are known to increase porosity. Depending on application and, thus, required morphology, different combinations of both suspending agents are used. It is quite obvious from formulation that suspension PVC contains limited amounts of additives which may complicate its further processing and its thermal and UV stability.

Polymerization is performed in large reactors (usually having a volume of up to 200 m^3). Considering that vinyl chloride is carcinogenic, most reactors are operated without opening. Several hundred batches can now be run without opening the reactor. This is due to excellent coating which prevents deposition of reacting mass on the reactor walls. It is also very important to control the temperature of reaction which is exothermic. The rate of heat removal is usually the rate controlling factor.

After reaction is complete, walls of the reactor are rinsed with water to remove any particles. If such particles are left in the reactor for the next batch, a monomer will be absorbed by them and polymerized within particles, resulting in non-porous particles which will cause formation of so-called “fish-eyes”. In addition, these particles will hold more vinyl chloride and increase its residual concentration in the final product. The reactor is coated with adhesion-preventive compound before a new batch begins. The reactor is charged again and reaction mixture is brought to a desired temperature to begin a new polymerization. Initiator used in suspension polymerization is monomer-soluble (unlike in emulsion polymerization, where it is water-soluble).

In the next operation, reaction mixture is stripped free of monomer to at least below 1 ppm. For a good stripping performance, polymer grains must be porous. In modern plants, steam stripping columns are used. In older plants, stripping is done directly in the polymer vessel or in the tank into which slurry is transferred after polymerization. The stripping temperatures exceed 100°C. The typical process time does not exceed 3 min. Holding polymer for longer times may cause its degradation and yellowing. The monomer recovered from this process is reused for the production of polymer.

Monomer-free slurry contains more than 50% water which is removed by centrifugation during which at least 60% of the water is removed. The effectiveness of water removal depends on the slurry temperature. At temperatures above glass transition temperature of PVC (82°C), more water is removed, most likely because the more elastic grains permit water removal from pores and interstices. Before transfer to dryer, antistatic is frequently added to prevent static formation during drying and resin use.

The most common dryers are a fluidized bed (for major grades) and rotatory (for shorter runs). Until moisture is present, temperature is below 100°C because heat is utilized for water evaporation. Close to moisture removal, temperature rises. Moisture removal is strictly controlled because a too large concentration of moisture may cause bubbling during processing, whereas too low moisture means longer exposure to higher temperature which may cause degradation and an increase in static formation, causing particles to stick to each other. Before PVC is packaged, it is screened in order to remove too large particles.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and concentration
- effect of polymerization temperature on molecular weight and polydispersity
- total conversion of monomer (defects types and their concentrations)
- selection of suspending agent(s) (particle size and porosity and thus conditions of stripping, centrifugation, and drying)
- size of polymerization reactor (ease of cooling which affects efficiency and molecular weight and its distribution)
- reactor wall coating and rinsing efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affect color and stability of resin)
- temperature of centrifugation (higher temperature increases effectiveness of centrifugation and thus reduces PVC exposure to heat)
- selection of dryer and its operating conditions (length of polymer exposure to elevated temperature)
- residual moisture level (potential bubbling, thermal degradation, antistatic properties).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

Near infrared spectroscopy was applied for monitoring of suspension polymerization process.[7] Use of calibration models permitted to predict and control the morphological properties of manufactured polymer by in-line monitoring.[7] The bulk density, the cold plasticizer absorption, and the average particle diameter were controlled.[7]

Morphological properties of suspension PVC were influenced by operation of condenser.[8] Delay in reflux operation increased cold plasticizer absorption, and decreased bulk density and K-value.[8] The commencement of refluxing before 20% conversion caused formation of bimodal particle size distribution (monomodal particle size distribution was obtained for longer delays).[8] This shows that operation principles have strong influence on properties of suspension PVC.[8]

Increase of final temperature of reaction and injection of additional reactant increased production output of suspension PVC by 19.1% without influence on resin quality.[9] This was accomplished by careful control of pressure and temperature in the reactor, and control of process variables.[9]

2.3.2 PASTE RESIN MANUFACTURING PROCESSES

Emulsion polymerization is the leading process of manufacture of paste-grade PVC. Microsuspension polymerization is also used for this purpose. We will briefly discuss both processes to show differences in technology and outcome. In the process technology, these two methods differ in the polymerization process, with all other unitary operations being the same.[6]

Paste grade producing plants are smaller and they are required to produce larger number of grades. Also, reactors are much smaller (20-80 m^3). The Huels plant having reactor with capacity of 200 m^3 is the only known exception.[6]

Unit operations include:

- charging, premixing, and homogenization (only microsuspension polymerization)
- charging and polymerization
- stripping
- spray drying
- separation, grinding, screening, and packaging.

Table 2.4 compares typical formulations for emulsion and microsuspension polymerizations.

Table 2.4. Typical formulations for microsuspension and emulsion polymerizations.[6,10]

	Concentration, parts	
	microsuspension	**emulsion**
Vinyl chloride	100	100
Water	137	110-180
Oils soluble initiator	0.2	-
Water-soluble initiator	-	1-1.2
Emulsifier	1	1-2

In microsuspension polymerization a mixture of vinyl chloride, water, emulsifier (e.g., alkyl aryl or alkyl sulfonate), and monomer-soluble initiator (e.g., lauroy peroxide) is homogenized in a separate vessel and pumped into the reactor. The mixture is then heated with agitation to the polymerization temperature. A stable emulsion with particle size of 0.1-5 μm is formed. This is in contrast to suspension or bulk polymerization which produces much larger particles (100 μm and above). Microsuspension polymerization differs from emulsion polymerization in the type of initiator used (oil or water soluble, respectively) and an additional operation used in microsuspension (homogenization), which is required to obtain regular, small particles.

In the case of emulsion polymerization, reaction begins in a water phase taking advantage of the fact that vinyl chloride is slightly soluble in water. Typical initiators of emulsion polymerization are ammonium and potassium persulfates and hydrogen peroxide. Polymerization continues in the monomer phase because polymer is not soluble in either monomer or water but monomer is very soluble in polymer (30 wt% monomer can be absorbed by polymer). Good control of particle size due to the use of proper mixing and effective emulsifier permits production of PVC with very narrow particle size distribution. Frequently, emulsion polymer is mixed in a production plant with microsuspension polymer which has a much broader particle size distribution. By such premixing, an adequate proportion of various particle sizes can be achieved in order to obtain a maximum packing density of polymer which reduces plasticizer demand (and viscosity) of PVC plastisols.

In the emulsion polymerization, the type and the quantity of emulsifier is the most crucial feature of the process which impacts particle size distribution of the resultant resin. Usually anionic emulsifiers are used and their concentrations are high compared with relatively pure suspension polymerizates. Unlike in other types of polymerization, emulsifier may not be added at the beginning but is metered throughout the process to control the rate of initiation and the size of particles (if more surfactant is added, more new growth sites are formed and particles become smaller). The rates of polymerization can be increased by the addition of reducing agents which increase the rate of initiation and help in reducing polymerization temperature.

Particle size distribution of emulsion polymerization can be further controlled by the so-called seeded emulsion polymerization. By choice of size and number of seed latex, the number of growth sites (particles) is controlled, giving superior control over particle size distribution. If combination of large and small particles is required, this is usually achieved by the use of a blending tank in which latices of different particle sizes are mixed prior to drying.

The polymerization reactor is protected against deposition of particles either by composition (glass lining or use of stainless steel reactors) or by a protective coating similar to suspension polymerization. Conversion of monomer for both microsuspension and emulsion polymerization is in the range of 80-90%. In the next step, reaction mass must be stripped of vinyl chloride. This is done by a combination of vacuum and temperature, most frequently in a reaction vessel but also in special tanks, columns, or thin film evaporators. If the temperature of the process is higher than the glass transition temperature of PVC (82^{o}C), polymer will begin to degrade. A slurry stripped to at least 8.5 ppm of vinyl chloride is transferred to dryer.

Slurry is pumped to a spray dryer where it is atomized into fine droplets falling into hot air. The selection of drying temperature (inlet and outlet temperatures) is important for quality since PVC without thermal stabilizers can be degraded and also agglomerated (if temperature is close to the glass transition temperature). The resin agglomeration also depends on atomizer tip speed. Atomizers are either equipped with a spinning disc or nozzle.[6] The performance of atomizer controls the size of the latex droplet and combination of inlet and outlet temperature and atomizer tip speed controls percentage of agglomerates. Higher atomizer tip speed produces a higher percentage of coarse particles. Inlet temperature increase causes an increase in the amount of agglomerates because more particles become fused. Similar effect has an increase in outlet temperature. Fine particles of paste resin tend to lump and cake, and for this reason bag shipment is more frequently used than bulk transportation.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and concentration
- effect of polymerization temperature on molecular weight and polydispersity
- total conversion of monomer (defects types and their concentrations)
- type and quantity of emulsifier
- size of polymerization reactor (ease of cooling which affects efficiency and molecular weight and its distribution)
- reactor wall coating and rinsing efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affect color and stability of resin)
- inlet and outlet temperatures in spray dryer
- atomizer tip speed (influences time of exposure to elevated temperature).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

2.3.3 BULK

Developed by Saint Gobain, later Rhone-Poulenc, and now Arkema (Lacovyl), the bulk (or mass) polymerization is the simplest process which uses only vinyl chloride monomer and initiator.[6] It does not require preparation of solutions, water, drying, separation, and waste water treatment. It is very efficient process, which, conducted in a small reactor, yields a large production output. It also results in the purest polymer because of simple polymerization formulation.

There are also many disadvantages, such as

- long heating required to strip residual monomer
- difficulties in cleaning off-gases (steam and/or nitrogen) from residual monomer
- problems with efficient wall coating and thus batch process is required
- production of fine particles which are difficult to handle
- complicated, two-stage process.

The last disadvantage is caused by the fact that during polymerization the reaction mixture changes from liquid to solid and it needs different conditions of mixing. The first commercial process in 1939 used a single reactor but sine 1962, two reactors are used: pre-polymerizer and post-polymerizer. In the pre-polymerizer, reaction is conducted up to 10% conversion, and in the post-polymerizer, up to 80% conversion of monomer. Since the first stage process is more efficient (reaction takes only 20 min), one pre-polymerizer is serving several post-polymerizers (initially horizontal but from 1978, vertical reactors).[6] Reaction temperature at the first stage is higher (usually 60-70°C) than in the second stage (usually 50-60°C). Initiators for the first and the second stage are different, considering temperature difference. The first stage produces seed particles and therefore controls particle morphology. The higher reaction temperature increases aggregation. Aggregation is also controlled by the type and quantity of initiator added in the first stage. Also, agitation speed helps to control primary particle size. The temperature of the second stage is selected to control molecular weight of the product. Second stage initiators have longer half-life time. Usually a combination of 2-3 initiators is used to obtain constant temperature of reaction. Material becomes powdery at about 20-25% conversion.[6] Final conversion of monomer is very important for porosity of particles. A high conversion rate will cause densification of particles and reduction of porosity.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and its concentration in each stage of polymerization
- effect of polymerization temperature on molecular weight and particle size
- total conversion of monomer (defects types and their concentrations)
- reactor wall coating and cleaning efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affects color and stability of resin).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

2.3.4 SOLUTION

If polymer is soluble in solvent, the polymerization reaction proceeds homogeneously. Because of a large chain transfer constant, molecular weight of PVC is also relatively low in solution synthesis. Solution polymerization is not used on a commercial scale because isolation of polymer requires evaporation of solvent, which is not safe and is expensive.

2.3.5 LIVING POLYMERIZATION

Living polymerization of vinyl chloride was patented.[11] The reaction can be initiated by a large number of initiators (for example, mono, di, tri or polyfunctional α,α-dihaloalkane, α,α,α-trihaloalkane, a perhaloalkane, a perfluoroalkyl halide, a polyfluoroalkyl halide, a benzyl halide, an allyl halide, a sulfonyl halide, an α-haloester, an α-halonitrile, an α-haloketone, an imidylhalide, or their combinations) in conjunction with non-metallic reducing single electron transfer reagents as catalysts (salts of dithionous acid, Na_2SO_3, formamidine sulfonic acid, and many others) and accelerated by electron shuttles (1,1'-dialkyl-4,4'-bipyridinium dihalide).[11] The process can be conducted at room temperature in water, producing PVC with a controlled molecular weight and narrow molecular weight distribution.[11]

Single Electron Transfer Degenerative Chain Transfer Living Radical Polymerization (a form of living radical polymerization) permits production of PVC on industrial scale.[12,13] The PVC manufactured by this method has different morphological features which cannot be obtained by conventional free radical polymerization.[12,13]

The above described living polymerization of VC permits production of low molecular weight polymer (M_n=20000) having high thermal stability (frequently better than the currently produced industrial products).[12] It is because much less defects are produced during polymerization and processing.[12]

2.4 POLYMERIZATION CONDITIONS AND PVC PROPERTIES

Polymerization has a profound effect on properties of PVC, including its thermal stability. In order to illustrate these influences, the results of some experimental studies and modelling are discussed below.

Size of reactor influences production output but at the same time increasing reactor size decreases surface area of walls through which reaction mixture can contact the heat exchanging medium. Figure 2.1 shows that the ratio of wall surface to the reactor volume decreases, which means that large reactors are more difficult to cool. Since VC polymerization is an exothermic reaction, a large amount of heat have to be removed in order to keep reaction temperature within process requirements.[6] Reaction temperature can also be controlled by the rate of initiator supply and the initiator properties (half-life temperature). It can be expected that a larger reactor will need to be run at slower rate to balance heat.

The diameter of particles depends on agitation speed (Figure 2.2).[14] There are many other parameters of reaction conditions which influence particle size. Figure 2.3 shows that the energy barrier between two primary particles decreases with particle size increasing.[15] The particle stability is estimated here based on the maximum height of repulsive

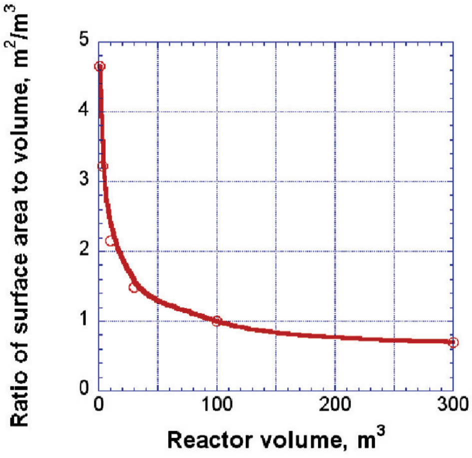


Figure 2.1. Ratio of wall surface area of reactor to its volume. [Data from Saeki, Y.; Emura, T., *Prog. Polym. Sci.*, **27**, 2055-2131, 2002.]

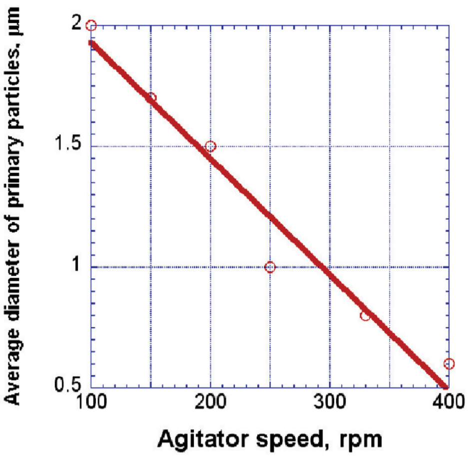


Figure 2.2. Average diameter of PVC primary particles vs. agitator speed. [Data from Zhao, J.-S.; Wang, X.-Q.; Fan, C.-G., *Polymer*, **32**, 14, 2674-2679, 1991.]

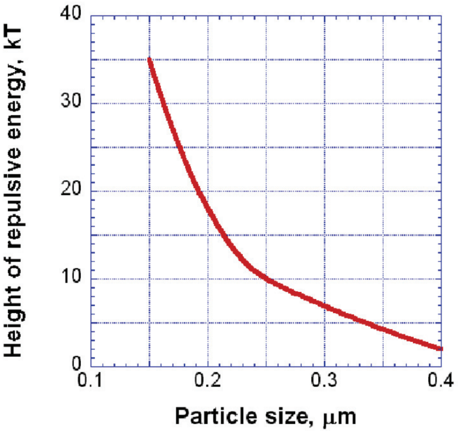


Figure 2.3. Particle stability as maximum height of repulsive energy barrier on particle approach vs. particle size. [Data from Tornell, B.; Uustalu, J. M.; Jonsson, B., *Coll. Polym. Sci.*, **264**, 439-444, 1986.]

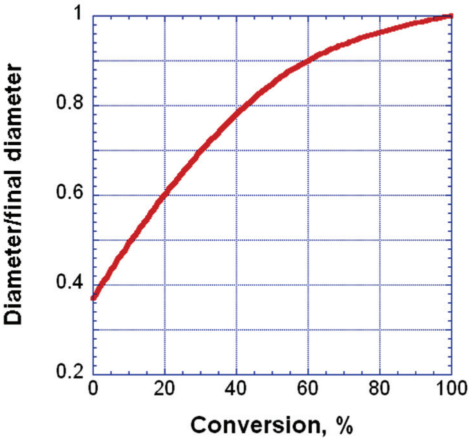


Figure 2.4. Relative mean particle diameter as measured by Coulter counter vs. conversion. [Data from Cebollada, A. F.; Schmidt, M. J.; Farber, J. N.; Capiati, N. J.; Valles, E. M., *J. Appl. Polym. Sci.*, **37**, 145-166, 1989.]

energy barrier on particle approach. This shows that larger particles are more likely to coalesce, which underlines the reasons for good mixing.[15]

Initial particles grow further during polymerization because monomer diffuses into primary particles but it is clear from Figure 2.4 that particle size is established very early in the process since further growth changes diameter only by up to approximately 150%.[16] Viscosity of reaction medium is known to contribute to the initial size of particles. Lower

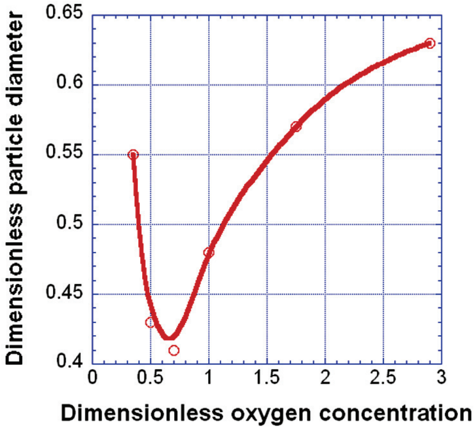


Figure 2.5. Effect of the initial oxygen concentration on the dimensionless average particle diameter. [Data from Kiparissides, C.; Achilias, D. S.; Frantzikinakis, C. E., *Ind. Eng. Chem. Res.*, **41**, 3097-3109, 2002.]

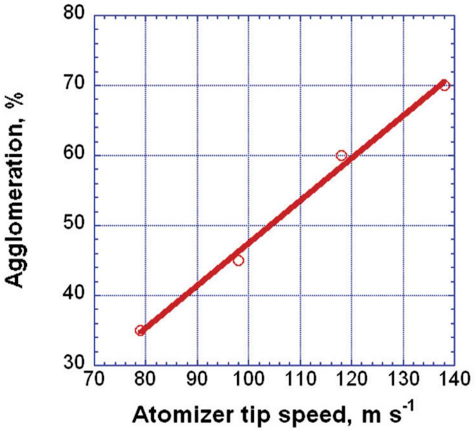


Figure 2.6. PVC agglomeration vs. atomizer tip speed in spray drying of emulsion polymer. [Data from Saeki, Y.; Emura, T., *Prog. Polym. Sci.*, **27**, 2055-2131, 2002.]

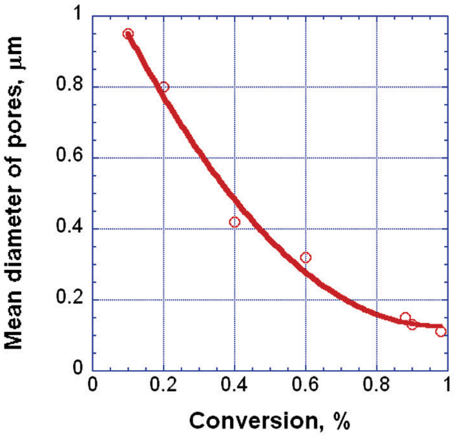


Figure 2.7. Mean pore diameter vs. conversion. [Data from Cebollada, A. F.; Schmidt, M. J.; Farber, J. N.; Capiati, N. J.; Valles, E. M., *J. Appl. Polym. Sci.,* **37**, 145-166, 1989.]

viscosity of reaction medium produces smaller particles.[16]

Oxygen is capable of reacting with initiator primary radicals and oligomers in the aqueous phase to produce vinyl polyperoxides.[17] The vinyl polyperoxides can decompose into radicals, which are capable of initiating new polymer chains. The average particle size exhibited a U-shaped behavior with respect to the initial oxygen concentration. This behavior is explained by the combined role of vinyl polyperoxides as radical generators and ionic strength promoters (Figure 2.5).[17]

Processes following polymerization also affect particle size, as seen from the example of drying emulsion polymerizate (Figure 2.6).[6] Not only atomizer speed but especially inlet and outlet air temperatures affect agglomeration and thus particle sizes. In addition, inlet and outlet temperatures cause initial degradation of PVC.

Pore diameter (Figure 2.7)[16] and porosity (Figure 2.8)[18] of particles decrease with conversion and/or polymerization time increasing. Similar is the case of specific surface area (Figure 2.9), which also decreases with conversion.[14] This is understandable considering that monomer diffuses into polymer grains and fills the available free volume.

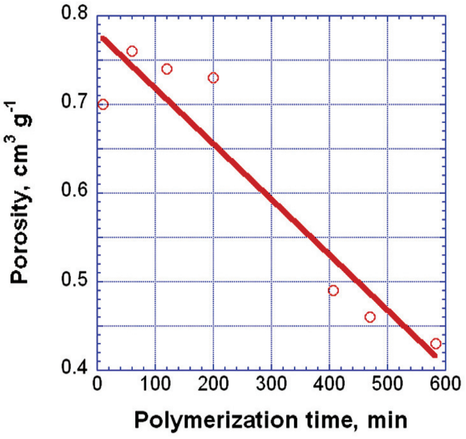


Figure 2.8. Porosity vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys*., **32**, 1, 99-109, 1994.]

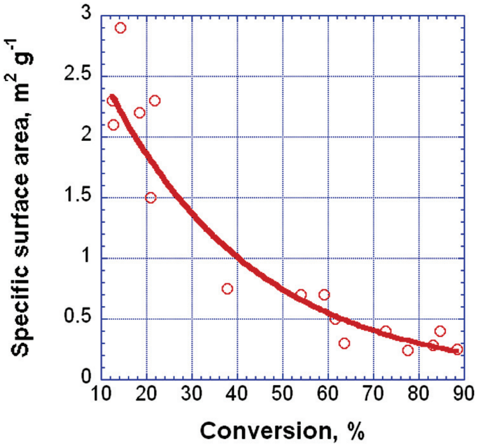


Figure 2.9. Specific surface area of PVC grains vs. conversion. [Data from Zhao, J.-S.; Wang, X.-Q.; Fan, C.-G., *Polymer*, **32**, 14, 2674-2679, 1991.]

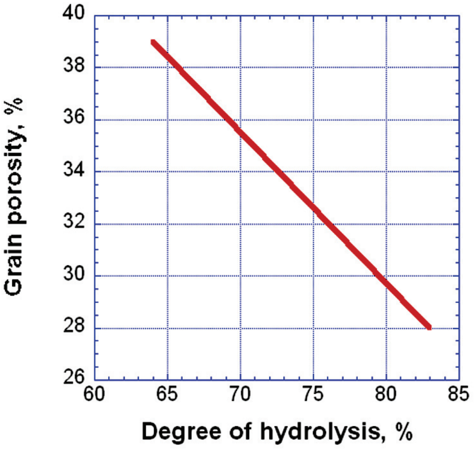


Figure 2.10. Effect of the degree of hydrolysis of PVAc on grain porosity. [Data from Zimmermann, H., *J. Vinyl Additive Technol.*, **2**, 4, 287-294, 1996.]

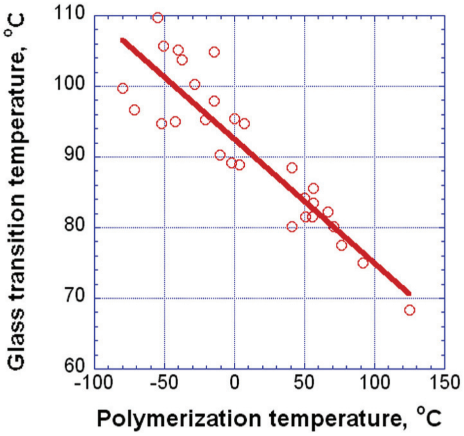


Figure 2.11. Glass transition of PVC vs. its polymerization temperature. [Data from Daniels, C. A., *J. Vinyl Technol.*, **1**, 4, 212-217, 1979.]

Porosity of suspension polymer depends also on composition of reaction mixture. Poly(vinyl alcohol) is frequently used as protective colloid. Poly(vinyl alcohol) is obtained by hydrolysis of poly(vinyl acetate). The degree of hydrolysis, in the range from 45 to 81.5%, affects porosity of PVC particles, as can be seen from Figure 2.10.[2]

Polymerization temperature affects glass transition temperature of polymer which is inversely proportional to polymerization temperature (Figure 2.11).[19] Figure 2.12 shows that glass transition temperature of polymer affects its processing properties.[20] The higher

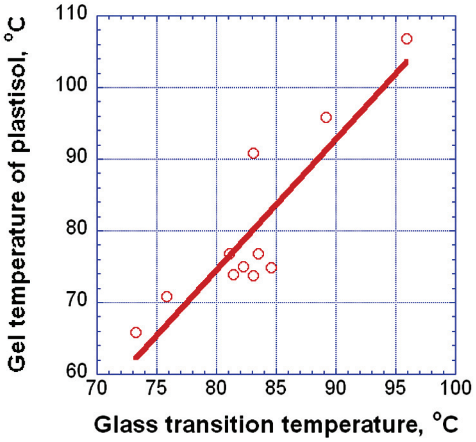


Figure 2.12. Relationship between gel temperature of plastisol and PVC glass transition temperature. [Adapted, by permission from Nakajima, N.; Yavornitzky, C. M.; Roche, E. J.; Harrell, E. R., *J. Appl. Polym. Sci.*, **32**, 1986.]

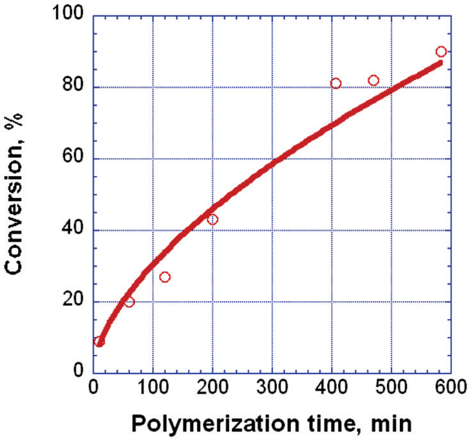


Figure 2.13. Vinyl chloride conversion vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys.,* **32**, 1, 99-109, 1994.]

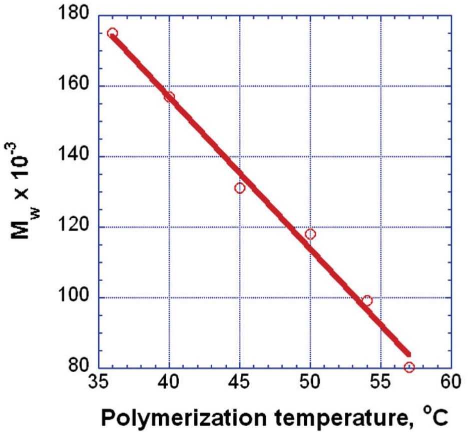


Figure 2.14. PVC molecular weight vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys*., **32**, 1, 99-109, 1994.]

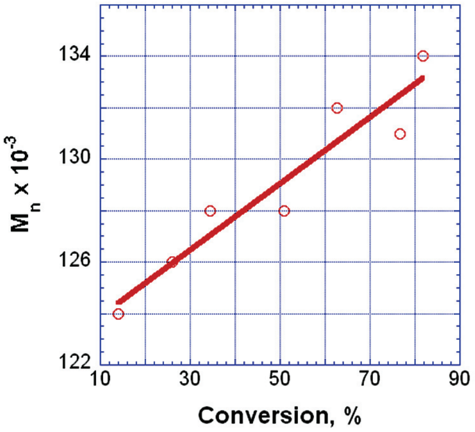


Figure 2.15. PVC M_w vs. monomer conversion. [Data from Bao, Y. Z.; Brooks, B. W., *J. Appl. Polym. Sci.*, **85**, 1544-1552, 2002.]

the glass transition temperature of polymer, the higher the gel temperature of plastisol. Polymers with higher glass transition temperatures require more heat to be processed.

The above influences are not surprising, considering that molecular weight of polymer depends on conversion and polymerization time (Figures 2.13-2.15). Increase in polymerization time under particular conditions increases monomer conversion (Figure 2.13).[18] Increase in polymerization temperatures causes an almost linear decrease in the

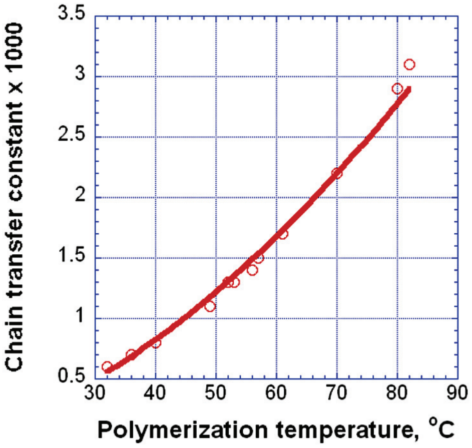


Figure 2.16. Chain transfer constant vs. polymerization temperature. [Data from Starnes, W. H., *Prog. Polym. Sci.*, **27**, 2133-2170, 2002.]

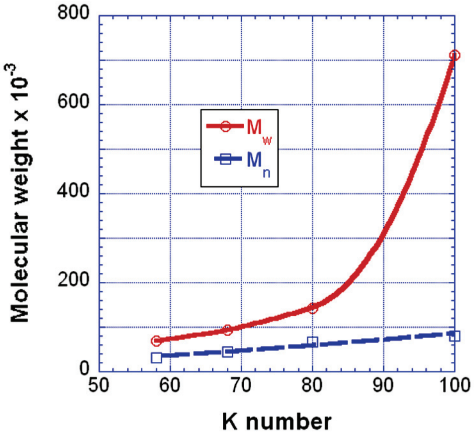


Figure 2.17. The relationship between molecular weight of PVC and its K number. [Data from Rogestedt, M.; Hjertberg, T., *Macromolecules*, **26**, 1, 60-4, 1993.]

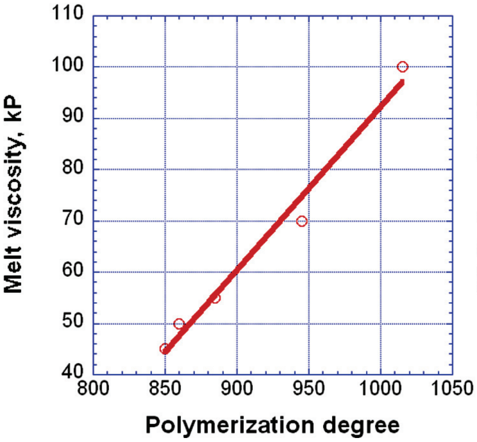


Figure 2.18. Effect of polymerization degree on melt viscosity. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.*, **25**, 1947-1951, 1990.]

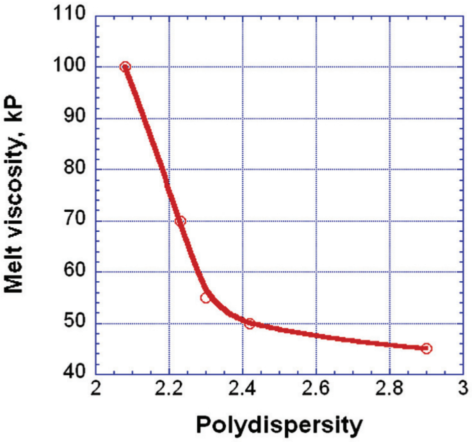


Figure 2.19. Effect of polydispersity on melt viscosity. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.*, **25**, 1947-1951, 1990.]

molecular weight of PVC (Figure 2.14).[21] Monomer conversion has smaller influence on molecular weight than the polymerization temperature (Figure 2.15).[21] It is so because the chain transfer constant is controlled by polymerization temperature (Figure 2.16).[22] K number correlates with M_n and M_w (Figure 2.17).[23]

Thermal treatment of PVC is related to its polymerization degree and polydispersity. Figures 2.18 and 2.19 show effect of polymerization degree and polydispersity on melt viscosity, respectively. Figures 2.20 and 2.21 show the effect of polymerization degree and

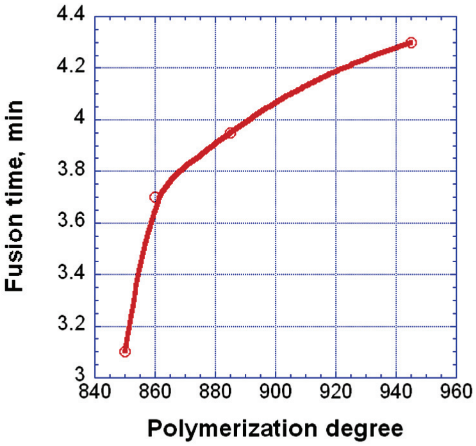


Figure 2.20. Effect of polymerization degree on fusion time. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.,* **25**, 1947-1951, 1990.]

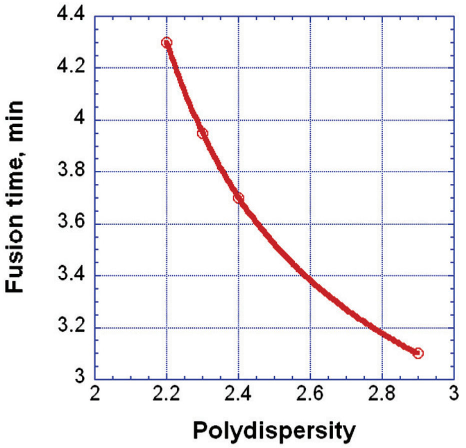


Figure 2.21. Effect of polydispersity on fusion time. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.*, **25**, 1947-1951, 1990.]

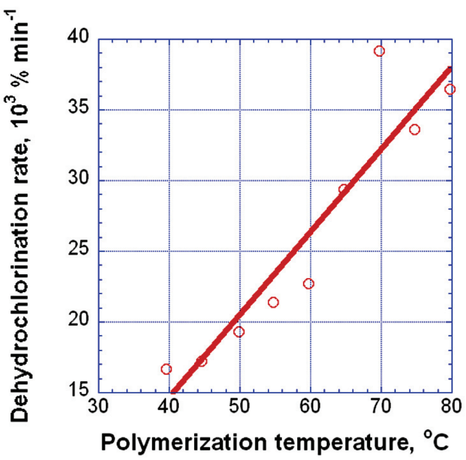


Figure 2.22. Influence of polymerization temperature on dehydrochlorination rate of PVC. [Adapted, by permission, from Xie, T. Y.; Hamielec, A. E.; Wood, P. E.; Woods, D. R.; Chiantore, O., *Polymer*, **32**, 9, 1696-1702, 1991.]

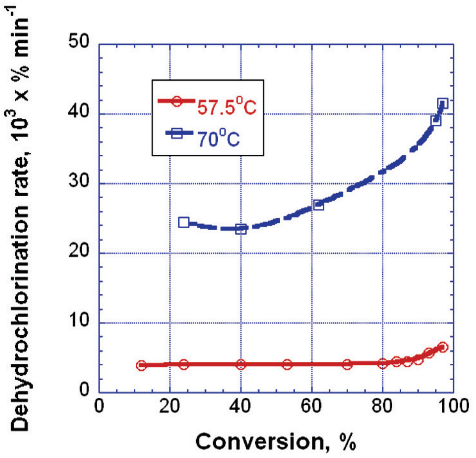


Figure 2.23. Effect of monomer conversion on PVC dehydrochlorination rate. [Data for polymerization at 57.5°C from Purmova, J.; Pauwels, K. F. D.; Van Zoelen, W.; Vorenkamp, E. J.; Schouten, A. J.; Coote, M. L., *Macromolecules*, **38**, 15, 6352-6366, 2005; data for polymerization at 70°C from Xie, T. Y.; Hamielec, A. E.; Rogestedt, M.; Hjertberg, T., *Polymer*, **35**, 7, 1526-34, 1994.]

polydispersity on fusion time, respectively. In both these cases as well as in the case of plastisol the gel time (Figure 2.12), molecular weight and its distribution control the amount of thermal energy required for processing by which they affect thermal stability of polymer.

The direct studies on polymerization temperature and conversion on thermal stability of PVC show that both have a strong effect. Increased polymerization temperature increases dehydrochlorination rate (Figures 2.22 and 2.23). In addition, after initial stages of conversion further polymerization decreases polymer stability (Figure 2.23) because of formation various defects as it was discussed in Chapter 1.

The data which were analyzed in this section show that PVC stability is influenced by conditions of polymerization. These influences together with the structural defects in PVC chain make behavior of PVC dehydrochlorination rate very complex.

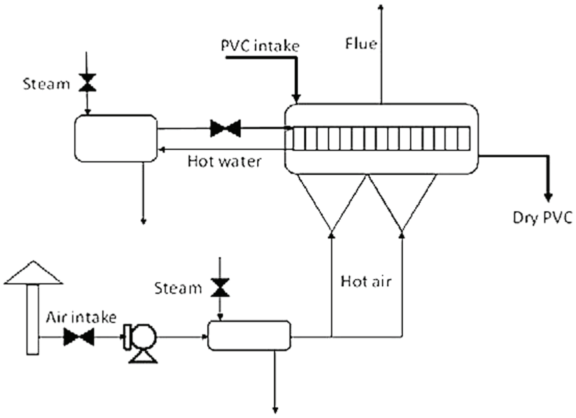


Figure 2.24. Schematic diagram of the continuous PVC fluidized bed drying process. [Adapted, by permission, from de Araujo, A. C B.; Neto, J. J. N.; Shang, H, 10th International Symposium on Process Systems Engineering - PSE2009.

2.5 OPTIMAL OPERATION OF INDUSTRIAL PVC DRYER

Several publications are now available on optimal operation of fluidized bed dryer for PVC.[27-29] Figure 2.24 shows a schematic diagram of fluidized bed dryer for PVC.[27] After polymerization, a mixture containing 30% PVC and 70% water is stripped of some water in a centrifuge, the remaining 20-30% water is removed in dryer shown in Figure 2.24. Temperature and outlet relative humidity are controlled in the dryer.[27] Proper control of temperature difference in the dryer allows to save 16% energy required for drying and to increase process output by 22%.[28] Numerical model was developed for control of drying operation.[29] Model further enhances economical operation of the dryer.[29]

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