INTRODUCTION TO PVC RESIN TECHNOLOGY

Only a small number of polymers with a particularly advantageous combination of properties have found a major place in commerce Although PVC as a polymer has found a significant position in today's marketplace, this polymer is chemically one of the least stable of the common polymers, and its exploitation came about only through the development of proper technology for handling the resin and the discovery of suitable stabilizers The factors responsible for the rapid growth of PVC are considered to be

- low cost
- the ability to be compounded into a wide range of flexible and rigid forms
- good physical, chemical, and weathering properties
- utility and a broad range of large volume application
- processability by a wide variety of techniques

Poly(vinyl chloride) (PVC) was first characterized more than 100 years ago, but did not start to gain commercial importance until the 1930s One of the earliest applications utilized a vinyl chloride-vinyl acetate copolymer as a coating for the interior of beer cans The problems caused by its inherently poor thermal heat stability were overcome by the development of suitable stabilizer systems Progress in PVC technology has involved a complex interaction between resin development, effects of additives, and equipment design, as well as market demands Today, PVC is the second largest volume thermoplastic used in the U S and is the lowest priced of the five leading plastics This low cost, along with its great versatility, is one of the major reasons for its large share of the plastics market

PREPARATION OF VINYL CHLORIDE

The phenomenal growth in PVC production has been largely due to the availability of low cost monomer Current commercial processes for production of vinyl chloride can be placed into two classes The first class involves the gas phase reaction of acetylene with hydrogen chloride using mercuric chloride or other heavy metal

$$HC{\equiv}CH + HCl \xrightarrow{HgCl_2} CH_2{=}CHCl$$

halides as catalyst The advantage of this acetylene process is that no hydrogen chloride is produced With the second class of processes, ethylene dichloride (EDC) is first produced by the reaction of ethylene with chlorine which is then subsequently pyrolyzed to yield vinyl chloride and hydrogen chloride Manufacturers employing the ethylene route with the resultant HCl by-product could combine this with the acetylene process in order to utilize the HCl

$$2HCl + \tfrac{1}{2} O_2 \longrightarrow Cl_2 + H_2O$$

$$Cl_2 + CH_2{=}CH_2 \longrightarrow CH_2Cl - CH_2Cl$$

$$CH_2Cl - CH_2Cl \xrightarrow{\text{heat}} CH_2{=}CHCl + HCl$$

Our Lake Charles Vinyl Chloride Monomer plant uses the newer oxychlorination process in which hydrogen chloride is oxidized using air or oxygen to produce chlorine in water The chlorine then reacts with ethylene to give you EDC This EDC is then pyrolyzed at higher temperatures to give you vinyl chloride plus HCl The HCl is then reacted with oxygen to convert it back to chlorine

PROPERTIES OF VINYL CHLORIDE

The following table lists the physical properties of vinyl chloride monomer Because vinyl chloride is gaseous at normal atmospheric temperatures, it is normally stored under pressure as a liquid

Color	Colorless, water clear
Odor	Pleasant, sweet
Molecular Weight	62 5
Boiling Point	-13 7°C
Freezing Point	-153 8°C
Density @ -20°C	0 983 g/ml
@ 20°C	0 910 g/ml
Refractive Index D15	1 398
Viscosity @ -20°C	0 274 cps
@ 25°C	0 193 cps
Surface Tension @ 20°C	22 27 dyn/cm
Flash Point, COC	-78°C
Explosive Limits in Air	4-22% by vol
Vapor Pressure @ 0°C	25 1 psi
@ 20°C	49 2 psi
@ 40°C	87 6 psi
Solubility of Water in VCM	0 11%
Solubility in Water @ 1 atm	0 5%
Heat of Polymerization	720 BTU/lbs

Vinyl chloride may be stored in ordinary steel cylinders, tank cars, and storage tanks Although vinyl chloride is stable under normal conditions, nevertheless, over a considerable period of time, polymer can build up in storage tanks and pipelines and, therefore, need to be inspected and cleaned at regular intervals Many problems caused by the presence of impurities in monomer have been largely eliminated Some of these impurities encountered are acetylene, iron, hydrochloric acid, oxygen, water, acetaldehyde, butadiene, and residual EDC

Under normal production routine, vinyl chloride is used without further purification However, even a trace of oxygen in the monomer will react to form peroxides, which may cause difficulties The initial reaction product appears to be a monomeric material soluble in the vinyl chloride monomer Subsequent decomposition or rearrangements lead to a polymeric peroxide of limited solubility which can initiate further polymerization The presence of trace amounts of water

and acid in the monomer accelerates this formation of peroxides and polymer Thus, it is quite necessary to maintain the monomer free of air, water, and acid, both to obtain the best quality resins and to minimize handling difficulties

CHEMISTRY OF VINYL CHLORIDE POLYMERIZATION

Vinyl chloride monomer (M) is polymerized efficiently in the presence of a free radical source (I•) The general reaction scheme and initial kinetics are typical of a free radical chain reaction and is shown below in Figure 1

- Initiation

$$I\text{-}I \xrightarrow{K_1} 2I\bullet$$

$$I\bullet + M \xrightarrow{K_2} IM\bullet$$

- Propagation

$$IM\bullet + M_x \xrightarrow{K_3} IM_xM\bullet$$

- Termination
  - Chain Transfer To Monomer

$$IM_xM\bullet + M \xrightarrow{K_4} IM_xM + M\bullet$$

  - Chain Transfer To Other Chemical

$$IM_xM\bullet + C \xrightarrow{K_5} IM_xM + C\bullet$$

Figure 1. The chemistry of vinyl chloride polymerization.

The rate of initiation (K_1 and K_2) is dependent on the type and concentration of initiator(s) and the temperature of polymerization The rate of propagation (polymerization, K_3) is also dependent on initiator(s) and temperature, but it becomes complex because of the presence of the precipitating polymer phase The molecular weight of the polymerizing PVC chain is dependent on the rate of termination (K_4) by transfer to monomer which is temperature dependent In addition, molecular weight can also be affected by chain transfer to another chemical (chain transfer agent), and this rate of termination (K_5) is dependent on temperature, type, and concentration of chemical additive Because K_5 is much greater than K_4, the resulting polymer chain will be of lower molecular weight

Experimental work has shown that the free radical polymerization of vinyl chloride is thought to strongly favor a head-to-tail structure The low order of crystallinity is attributed to the non-regular positioning of the chlorine and hydrogen atoms about the carbon atom The degree of crystallinity of commercial PVC is estimated to be about 8-10% Chain branching is believed to be low What branching does exist is attributed to free radical transfer from a growing chain to the back of the same or another polymer molecule

$$\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}$$

Four types of processes are used for the commercial manufacture of PVC suspension, mass, emulsion, and solution polymerization About 83% of all PVC is

produced by the suspension process, about 8% by the mass process, about 8% by the emulsion process, and about 1% by the solution process

SUSPENSION POLYMERIZATION PROCESS

The suspension polymerization process involves the mechanical dispersion of vinyl chloride in an aqueous medium Suspending agents, or protective colloids, which are water soluble polymers are used to help stabilize the monomer droplets Monomer soluble initiators, such as peroxypercarbonates, peresters, and peroxides, are used to initiate the polymerization

Figure 2 illustrates a typical suspension PVC process flow diagram The process begins with the charging of the process ingredients, as shown in Figure 3 While being agitated, the mixture of these ingredients is brought to the desired polymerization temperature, usually by circulating hot water through the reactor's jacket Since the polymerization of vinyl chloride is an exothermic reaction, the heat of reaction must be removed in order to maintain the desired polymerization temperature This heat can be removed by circulating cooling water through the reactor jacket Refrigerated water and specially designed cooling baffles can improve heat removal Also, stainless steel-lined carbon steel reactors have an advantage over solid stain-less steel or glass-lined reactors Several producers have developed reflux condenser technology to improve the reactor's heat removal capacity

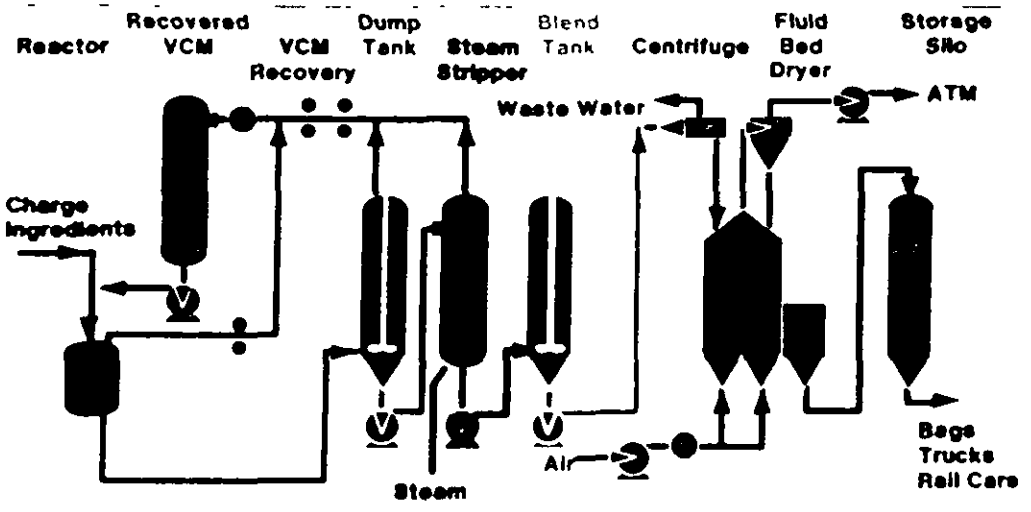


Figure 2 Typical suspension PVC process flow diagram

Ingredients	Parts By Weight
Vinyl Chloride	100
Process Water	150
Suspending Agents	0 05
Chemicals	0 01-2 0
Initiator	0 06

Figure 3 Typical suspension PVC recipe

The pressure in the reactor is the sum of the partial pressures of vinyl chloride and water at the polymerization temperature

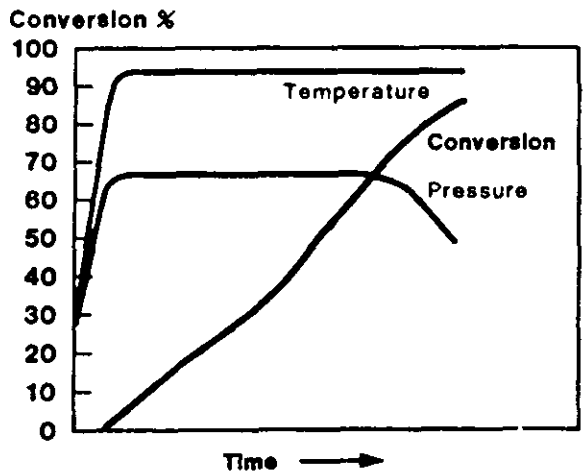


Figure 4. Conversion rate for vinyl chloride polymerization.

As shown in Figure 4, the temperature and pressure remain constant during polymerization up to about 70% conversion, at which time the reactor pressure begins to drop because of the absence of liquid monomer The rate of conversion increases throughout the polymerization, but begins to decrease at pressure drop The polymerization time is dependent upon the amount of initiator charged The reaction is then terminated at a specific conversion depending on product quality requirements The unreacted monomer and PVC slurry are then transferred to a dump tank, and the unreacted monomer is degassed into the recovery system and stored in a separate tank to be recycled back into the reactor with the other charge ingredients

The discovery in 1973 that exposure to vinyl chloride resulted in the increased incidence of a rare form of liver cancer (angio-sarcoma) resulted in fundamental changes in the PVC industry In addition to air emission and water discharge regulations in general, PVC producers must now comply with OSHA employee vinyl chloride exposure standards and the EPA vinyl chloride emission standards These standards are met by additional monomer recovery in a stripping process where the slurry is heated and stripped of very small amounts of residual vinyl chloride by contact with steam Continuous steam stripping is carried out in a trayed stripping tower by injecting steam directly into the slurry This stripping process is carried out in such a way as to minimize heat exposure of the resin to avoid resin degradation

The reactor is then rinsed with water In order to meet OSHA and EPA regulations, employee exposure and reactor opening emissions are eliminated by using high pressure water-cleaning equipment that operates in a closed reactor Then the reactor's internal surfaces are treated with chemicals to prevent polymer buildup The reactor is then ready to be recharged Although the suspension polymerization of vinyl chloride is a batch process, after the reactor is emptied, the down-stream processes can be carried out in a continuous manner

The stripped slurry is then held in a blend tank before being centrifuged to produce a wet cake having a water content of 18-25% A two-stage fluid bed

dryer is used to dry the resin to below 0.3 wt% water. The resin is then stored in silos and is usually shipped in bulk by either rail cars or trucks, or packaged in bags or gaylords.

PVC plants before the 1970s contained many small batch reactors. Large reactor technology allowed the reactor size to be increased from 2,000-10,000 gallons to 15,000-50,000 gallons. These large reactors increased productivity, lowered plant costs, improved product quality and uniformity, and reduced vinyl chloride exposure and emissions. More and more older small reactors have been shut down and replaced with modern large reactors.

MORPHOLOGY OF PVC

In the suspension polymerization of vinyl chloride, the bulk monomer phase is dispersed in water by vigorous agitation, and the droplets produced are stabilized by the presence of a suspending agent. The correct amount of this suspending agent is used so that the monomer droplets undergo controlled coalescence during polymerization to give rise to an irregularly shaped grain having an average particle size of about 150 microns (Figures 5 and 6) The size, shape, and porosity of this grain is very dependent on the type and concentration of the suspending agent used and on the type of agitation (e g stirrer speed, agitator type, size and shape of baffles)

Microscopic examination of this PVC grain shows it is composed of an agglomeration of **sub-grains** which are about 40 microns in average size (Figures 7 and 8) These are the stabilized monomer droplets which, during the initial phase of polymerization (about 5-15% conversion), coalesce to form the PVC grain Further microscopic examination of these sub-grains show they are made up of primary particle **agglomerates** which are about 5 microns in average size (Figure 9) These are formed during the early stages (2-5% conversion) of polymerization by coalescence of **primary particles** These primary particles are about 0 7 microns in size and are formed at very low conversion (less than 2%)

Within the monomer droplet suspended in the water, the first aggregate of polymer chains that precipitate, about 50 in number, form the smallest PVC species identified so far, the **microdomain**, which is about 0 02 microns in size These microdomains coalesce to form a **domain** A domain is the nucleus of the primary particle, contains about 1,000 microdomains, is about 0 2 microns in size, and is only observed at very low conversions (less than 2%) This term is only used to describe the 0 2 micron species because it immediately starts to grow to become the primary particle The microdomain and domain are not features of PVC morphology at high conversions since a growth of these species with conversion obliterates all memory of them, leaving only the observable primary particle

From this discussion, it can be shown that the formation of suspension PVC takes place through a series of interconnected aggregation steps which can be represented by the scheme in Figure 11

Suspension PVC particles usually possess a pericellular "skin" or "membrane" which extends almost continuously over the entire outer surface of the grain This skin is formed during the early stages of polymerization (less than 5% conversion) and has been shown to be a copolymer of vinyl chloride and the suspending agent(s) Since this skin is semi-permeable, it does contribute to the overall porosity of the resin, but not nearly to the extent as does the primary particle agglomerate

Several different types of PVC grains can be obtained during the suspension polymerization process The most desirable grain has a semi-permeable skin and good porosity where the pores are open and evenly distributed throughout the grain A less desirable grain contains closed pores which are not connected to the skin The least desirable grain is the solid grain containing little or no porosity The production of these different types of grains is mainly determined by the choice of suspending agents

REACTOR PROCESS VARIABLES AFFECTING THE PROPERTIES OF SUSPENSION PVC

Molecular Weight

The various different grades of commercial PVC are mainly determined by their molecular weight In the absence of other active chemicals, the molecular weight of PVC is almost entirely determined by the polymerization temperature, the higher the polymerization temperature, the lower the molecular weight

In the presence of chain transfer agents, the molecular weight is lowered depending on the type and concentration of agent Thus, low molecular weight resin can be produced at lower polymerization temperatures using chain transfer agents In the opposite manner, the use of chain extending agents will allow the production of high molecular weight resins at higher polymerization temperatures

Particle Size

Particle size is important for various PVC applications For rigid extrusion, a more coarse resin is desired so that all of the grains are well fused in the extruder and no unfused fines are left to cause weaknesses in the final product For plasticized applications (calendering, blown film), a finer resin is preferred so that there are no large unfused grains which will cause imperfections in the finished product.

Within a given reactor with a given agitation system, the particle size of PVC is dependent upon the type(s) and concentration(s) of the suspending agent(s), the higher the concentration of suspending agent(s), the finer the resin Since the PVC grains are a distribution of sizes, particle size is usually described as an average particle size and the broadness (or narrowness) of the distribution is described as the coefficient of variation (the standard deviation divided by the average particle size), the smaller the coefficient of variation, the more narrow the particle size Particle size can also be expressed as the percent through a set of standard mesh screens (ASTM test method D-1705-82).

Porosity

The porosity of PVC is most important in controlling not only the absorption of plasticizers but also the desorption of vinyl chloride during the recovery/steam stripping process A good understanding of the mechanism for the development of porosity in PVC is necessary to insure good quality resin The various grades of PVC can be further divided into porous (for flexible applications) and non-porous (for rigid applications) resins

The process of plasticizer absorption is generally believed to occur by a diffusion mechanism in which two separate mechanisms exist The first process is a very rapid capillary filling of the intergrain (pores between the resin grains) and intragrain (pores within the resin grains) pores The second process involves the diffusion of the plasticizer molecules into the molecular PVC chains This second process is the rate-determining step in the absorption of plasticizer and is controlled by the size of the sorbing sphere, the primary particle agglomerate

Since it is known that one way to increase the absorption rate of a fluid into a solid is to reduce the size of the solid particle, it can be concluded that as the diameter of the agglomerate increases, the porosity of the resin decreases Thus, controlling the size of the agglomerate is the important step in establishing the porosity of a PVC resin

There are several process variables that affect the porosity of PVC These are as follows

Polymerization Temperature - For a given set of polymerization conditions, reaction temperature has a very large effect on porosity, the higher the reaction temperature, the lower the porosity This is because the agglomerate size increases as the reaction temperature increases

Conversion - Conversion is also found to have a very large effect on resin porosity, the higher the conversion, the lower the porosity Again, this is due to the agglomerate size Resins polymerized to a higher conversion have larger agglomerates than those polymerized to a lower conversion

Agitation System - Agitation is of fundamental importance in the PVC suspension process Together with the suspending agent system, it determines the particle size of the finished product and other properties, such as porosity Generally, the more power (e g higher speed) the agitation system puts into the reaction mixture, the higher the porosity Also, different agitator blades and baffles can affect resin porosity

Suspending Agent System - Given a particular type of agitation system, a particular polymerization temperature, and a reasonable conversion (75-85%), the suspending agent system has a great influence on resin porosity The **primary suspending agent** is usually a water soluble organic polymer, such as a polyvinyl alcohol, a substituted cellulose, or a mixture of the two Generally, the lower the surface tension of the suspending agent(s), the higher the porosity of the resin

The primary suspending agents are chosen not only for their ability to control particle size but also for their ability to produce porous resin However, the degree of surface activity for these chemicals is limited, thus additional **secondary suspending agents** are used to further increase porosity A variety of materials can be used, such as nonionic or anionic surfactants and low molecular weight polyvinyl alcohols of very low degree of hydrolysis These secondary suspending agents increase porosity by either lowering the surface tension between the vinyl chloride and the aqueous phase or by stabilizing the primary particle agglomerates during polymerization

There are several ways of measuring and expressing the porosity of PVC Among these are the following

Porosity - This is measured by mercury intrusion and expressed as cc/g (ASTM D-2873-70) Also other descriptions of the porosity of the resin are available from this single measurement void volume (cc/g), a

measurement of the intergrain pores (volume between the resin grains), average pore size (microns), a measurement of the diameter of the pores within the grain, and distribution of pore sizes

Cold Plasticizer Absorption (CPA) - The amount (%) of plasticizer that a resin will absorb at room temperature (ASTM D-3367-75) This is a measurement of both inter- and intra-gram porosity and should be about the same value as the mercury intrusion porosity measurement

Brabender Dry Time - Under a given set of test conditions, this measures the time (min) that it takes a given amount of resin to fully absorb (giving a dry powder) a given amount of a particular plasticizer at an elevated temperature (about 80°C) using a torque rheometer for mixing (ASTM D-2396-79) This is primarily a measure of the filling of the inter- and intra-grain pores and the rate of hot plasticizer absorption (diffusion into the resin molecules), but measures, to some extent, the capacity of the resin for plasticizer

Gel Test - In this test, a plasticized milled sheet is prepared under given conditions and the number of gels (fisheyes, hard particles, glassies) are counted in a given area (ASTM D-3596-77) A gel is a PVC grain which does not absorb plasticizer at the same rate as the other grains This is usually due to the inaccessibility of the pores to the plasticizer The number of gels will decrease to a constant number as the length of time on the mill increases

Microscopic Examination - A simple technique for qualitatively examining the porosity of PVC is placing the resin on a microscope slide and immersing it in a liquid having a refractive index similar to PVC and, after equilibrium, viewing it at low magnification (100x) with transmitted light The internal morphology of each grain can clearly be observed

Bulk Density

Generally, the bulk density (g/cc) of PVC (ASTM D-1895-69) is in opposition to its porosity, as porosity decreases, bulk density increases Thus, all of the process variables that affect porosity also affect bulk density The most important process variable is probably the choice of the suspending agent system

For rigid extrusion applications, the rate of output of the extruder (especially twin-screw extruders) is directly dependent on the bulk density of the dryblend which feeds the extruder Thus, it is important that this dryblend have a high bulk density

Electrical Properties

For wire and cable applications, the electrical conductance of the PVC resin is an important property PVC must be produced which has extremely low conductivity (or very high resistivity) Generally, this is done by using deionized (DI) water as the process water and not contaminating the resin with non-DI water or resin made with non-DI water

STEAM STRIPPING AND DRYING PROCESS VARIABLES AFFECTING THE PROPERTIES OF SUSPENSION PVC

Color

The color of PVC resin is usually measured by a colorimeter and is described by a L-, a-, and b-value The L-value is a measure of its whiteness, the a-value is a measure of its pinkness, and, the b-value is a measure of its yellowness In order to assure a white, non-pink, non-yellow resin, antioxidants and killing agents (to prevent further polymerization at high temperatures) can be added to the slurry before steam stripping and drying to prevent degradation

Heat Stability

Good heat stability of PVC is maintained by the proper care given to the steam stripping and drying processes Too high a temperature or too long a residence time will decrease resin heat stability Again, the addition of antioxidants and killing agents will aid in maintaining good heat stability

Heat stability is usually measured in these three ways

Static Oven Heat Stability - PVC is milled into a given plasticized compound and subjected to a given temperature in an air-circulating oven Coupons (or chips) are removed from the oven over a given period of time until the milled sheet has degraded to black (ASTM D-2115-67) The resins are compared to a standard resin of the same molecular weight and similar quality If the time-to-black is less than the standard resin, then the heat stability of that resin is poor

Dynamic Mill Heat Stability - PVC is mixed into a given rigid dryblend and placed on a two-roll mill at a given speed and temperature Coupons (or chips) are removed from the mill at given intervals of time until it turns dark or sticks to the mill Again, the resins are compared to a standard and judged to be less stable if the milled sheet turns dark or sticks to the mill before the standard

Brabender Heat Stability - PVC is mixed into a rigid dryblend and placed in a torque rheometer at a given speed and temperature The amount of time it takes from fusion to degradation is a measure of its heat stability

Percent Volatiles and Contamination

Both of these properties are mainly dependent on the proper use of the dryer If the dryer temperature is too low, then an excess of volatiles will be present in the resin if the dryer temperature is too high, the amount of contamination (dark specks which are usually burnt resin) will be too high Also, contamination can be caused by a dirty dryer

Static

Even if the PVC is dried to the proper dryness, there may be static built up on the resin which will cause poor flow properties The static can be eliminated or reduced in the drying process by the addition of an antistatic agent (e g, dry steam)

MASS POLYMERIZATION PROCESS

Elimination of the requirements for suspending agents and other additives prompted considerable effort to develop a suitable commercial process to polymerize vinyl chloride by a mass process Extensive research efforts were undertaken during the 1940s and 1950s to develop a successful mass polymerization process because of its potential for both cost savings (reduced raw material usage and elimination of the centrifuging and drying operations) and product improvement (reduction of chemical residues and elimination of the pericellular skin) Initial attempts followed the fairly conventional approaches of using a single reactor A major breakthrough came in 1963 when Pechiney-Saint Gobain (later to become a part of Rhone-Poulenc and now a part of Chloe Chemie) developed a two-stage process Licensees are now producing PVC by this patented process in Europe, Japan, United States, and other countries

The first reactor is vertical and fitted with a high intensity turbine-type agitator to give vigorous agitation to obtain the desired particle-size distribution Only monomer and initiator are charged, and polymerization proceeds to about 10% conversion at which point the formed particles are dispersed in the bulk of the liquid monomer as a sort of PVC slush in monomer A monomer soluble initiator is used, and the particle size is controlled by the speed of the agitation Then the free-flowing mass is transferred to a horizontal reactor fitted with a "ribbon blender"-type agitator More monomer and initiator are added and the polymerization continues being slowly stirred At about 20% conversion, all of the liquid unpolymerized monomer is absorbed into the porous structure of the grains leaving only a dry powder The second reactor is about twice the size of the first which feeds up to five second-stage reactors The heat of polymerization is removed through reflux condensers, and polymerization continues to about 70-80% conversion The unreacted monomer is recovered, followed by high temperature stripping, and the reactor is emptied by means of an air flow The product is transferred to a large classification system which screens out the oversize particles (about 3-8% of the yield) and then is transferred to silos without the need for centrifuging or drying

Continuous updating of the process has occurred with a progressive increase in reactor size A very significant development has recently occurred with the introduction of a vertical second-stage reactor which is easier to empty and clean, produces less oversize particles, and gives higher-quality product

PROPERTIES OF MASS PVC

PVC grains produced in the mass process are very round and uniform in nature They have the same morphology as suspension PVC grains except for the semi-permeable skin They have an average particle size about the same as suspension PVC, but have a very narrow particle-size distribution Since there is no suspending agent present, they do not have a pericellular skin, as seen in Figure 10 They have about the same porosity as suspension PVC and the same reaction variables (except suspending agent) affect porosity (e g polymerization temperature, conversion, agitation) Chemicals can be added to increase porosity and also to improve heat stability

A very positive feature of mass PVC, especially in rigid extrusion applications, is its high bulk density resulting in a high dryblend bulk density which gives high extrusion rates In the U S, most of the mass resin is used in rigid applications

Mass PVC is very similar to suspension PVC, and they compete in almost the same application areas, however, they are not compatible Mixing the two leads to powder-flow problems Thus, they must be used separately and can not be mixed in the same storage silos

EMULSION POLYMERIZATION

As in suspension polymerization, emulsion polymerization involves the dispersion of vinyl chloride in an aqueous medium The most important characteristics of an emulsion process as distinguished from suspension polymerization are the use of wetting agents or soaps as emulsifying agents and a water-soluble initiator Agitation, though necessary, is not as important as it is in a suspension process since the soap is present to maintain an emulsion or latex Protective colloids are usually used to ensure latex stability The PVC particles obtained by the emulsion technique are about one micron in diameter, which is about 100 times smaller than those made in the usual suspension process As in a suspension process, there is a distribution of particle sizes Also, as in the suspension polymerization technology, the amount of emulsifier will affect the final size of the latex particles

Emulsion polymerization may be described in the following manner At the concentration employed, most of the soap exists in the form of micells These tiny micells serve to stabilize a portion of the vinyl chloride which is only slightly soluble in the water The remainder of the monomer exists as small droplets A free radical generated from the water-soluble initiator enters the micell, meeting a monomer-rich environment, and a rapid polymerization takes place on a small scale Polymerization, therefore, takes place primarily in the monomer solubilized in the soap micells rather than in the dispersed droplets of monomer because the free radical formed by the initiator goes into these micells As polymer forms, the monomer in the micells is replenished by migration from the droplets, thus, the emulsion polymerization can be described as taking place in the water phase rather than in the monomer-droplet phase As these micells grow and the further polymer is produced, these small particles are then protected by the soap used for the polymerization When the polymerization is complete, which is usually at about 30 percent solids, the residual monomer is removed, and the latex is generally spray-dried to give a fine powder which is packaged

SOLUTION POLYMERIZATION

The Union Carbide Corporation was responsible for the development of solution polymerization techniques for vinyl chloride/vinyl acetate copolymers The methods employed produce highly uniform copolymers of various molecular weights Applications are mainly solution coating resins where the high quality and uniformity justify the higher manuafacturing cost

Polymerization is carried out in solvents in which the polymer is insoluble, resulting in precipitation of the resin during polymerization These copolymers do not contain suspending agents and are also free of homopolymer impurities

COPOLYMERIZATION

In the copolymerization of two monomers, either monomer can add to itself or the other monomer present The composition of the copolymer obtained from a specific mixture of monomers is determined by the two reactivity ratios of the corresponding monomers The polymer thus formed at any instant will be different from the monomer mixture Where the reactivity ratios of each monomer are both less than one, the polymer tends to alternate If one of the reactivity ratios is greater than 1, and the other reactivity ratio is less than 1, the polymer will be richer in monomer of the reactivity ratio greater than 1 To prevent formation of a polymer with a wide distribution of composition, it is generally necessary to add the more reactive monomer during the course of the polymerization

The limitations of PVC, as recognized early in its development, led to efforts for modification by copolymerization Improvements were required in heat stability, melt viscosity, solubility, and processing temperature Copolymers have thus become an important part of the total consumption PVC The chloride-vinyl acetate copolymer predominates as the most useful copolymer of vinyl-chloride, and its applications include coatings, floor coverings, and phonograph records The vinyl acetate content of most commercial copolymer ranges from 1/2 to 15 percent The greatest flexibility in solubility is obtained at the higher levels The major applications for the vinyl chloride/vinyl acetate copolymers are those in which low melt viscosity, low processing temperatures, freedom from external plasticizers, and solubility are required

The reduction in melt viscosity and increased flexibility are attributed to interference by the bulky acetate groups with intermolecular associations Copolymerization with vinyl acetate reduces tensile strength, heat distortion temperature, chemical resistance, abrasive resistance, and heat stability Another important group of copolymers is that formed by the copolymerization of vinyl chloride with olefins The introduction by Air Products of a vinyl chloride-propylene copolymer is directed towards improved processing characteristics, permitting higher production rates and a lower processing temperature The reduced processing temperature allows lower stabilizer requirements and permits less expensive nontoxic stabilizers for application, such as blow-molded bottles The propylene content in this copolymer is about 3 to 5 percent These copolymers have been approved by the FDA for food applications and may be used for packaging at temperatures up to 150°F

Another modified PVC which is not strictly a copolymer is chlorinated PVC An early attempt to change the chemical structure of PVC to improve processibility, solubility, and heat stability was through chlorination Chlorinated PVC is obtained by chlorinating PVC particles in a water suspension A patent was issued to B F Goodrich describing this process

REFERENCES

Since this is only meant to be an introduction to PVC resin technology, a complete bibliography is not included If the reader is interested in further pursuing this subject matter, then the following references will be very useful and current If the reader wishes to delve even deeper into the literature, these books have many more references than what would have been found here

R H Burgess, Manufacturing and Processing of PVC, MacMillan Publishing Co , Inc , 1982

G Butters, Particulate Nature of PVC, Formation, Structure and Processing, Applied Science Publishers, Ltd , 1982

W V Titow, PVC Technology, Fourth Edition, Elsevier Applied Science Publishers, 1984

Figure 5. Suspension PVC grains: 50X.

Figure 6. Suspension PVC grains: 250X.

Figure 7. Suspension PVC grain: 800X.

Figure 8. Interior structure of a suspension PVC grain: 800X

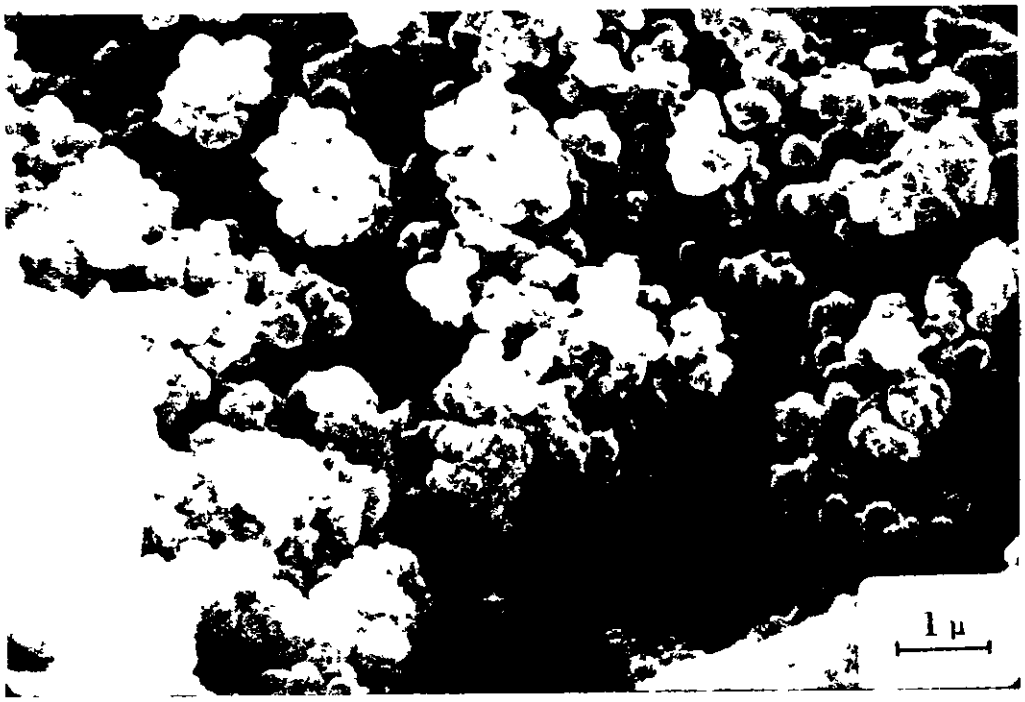


Figure 9. Interior structure of suspension PVC grain: 10,000X

Figure 10. Mass PVC grain: 250X

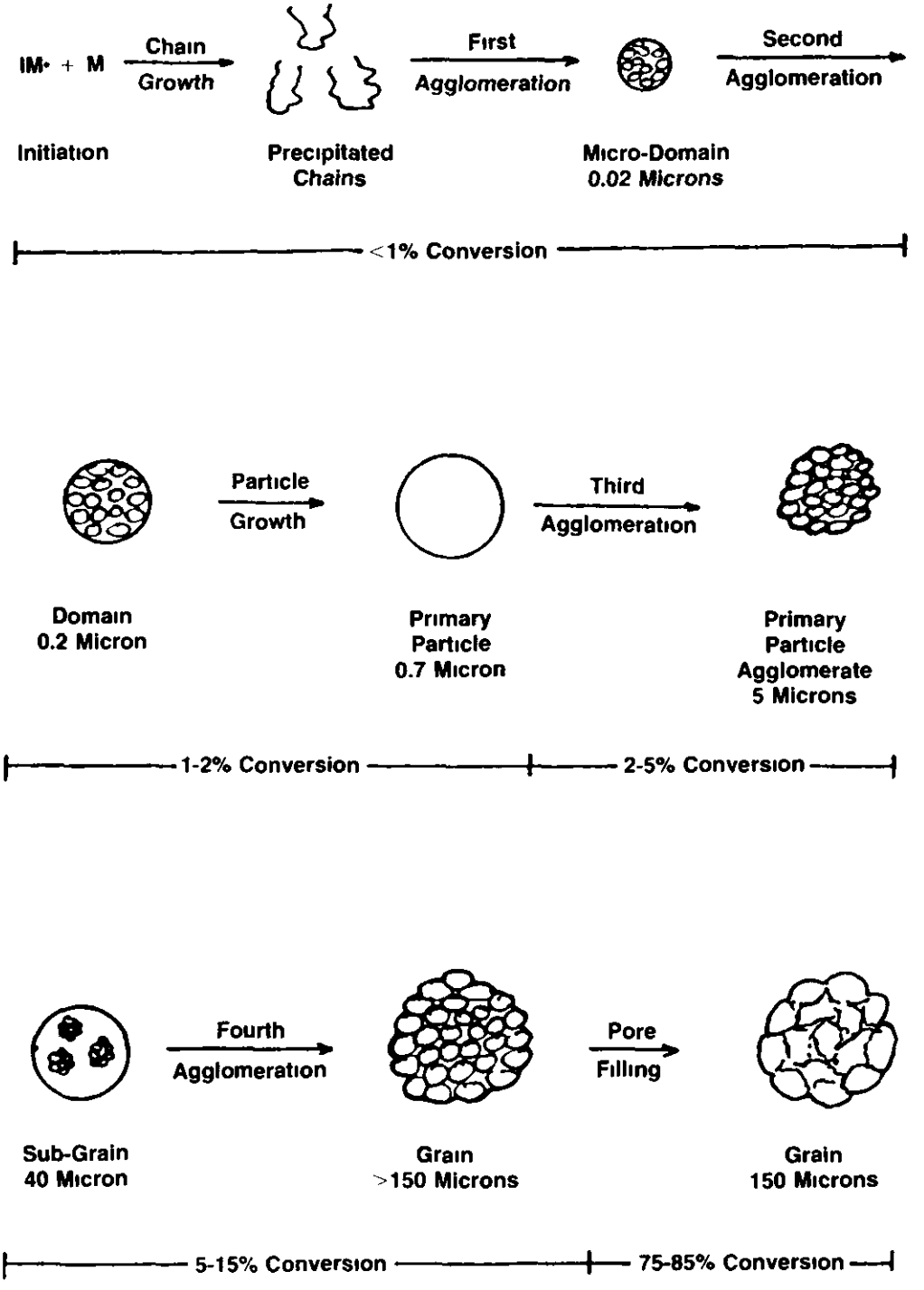
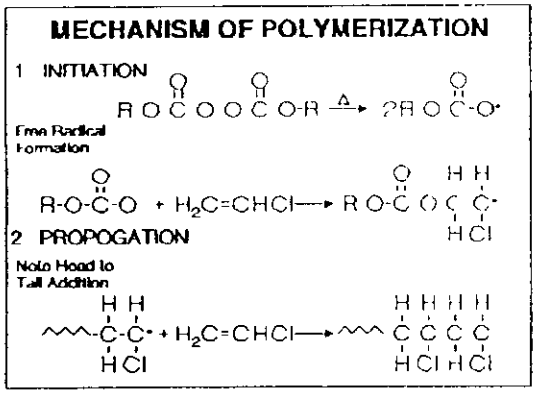
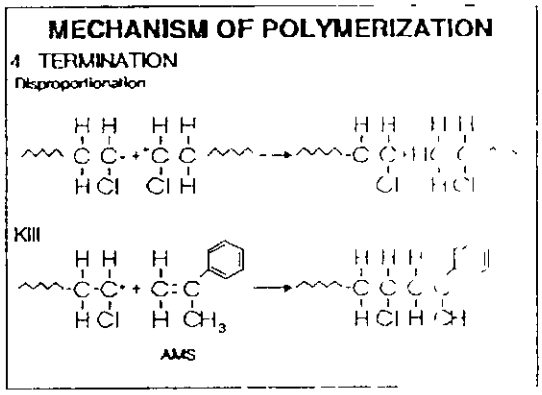


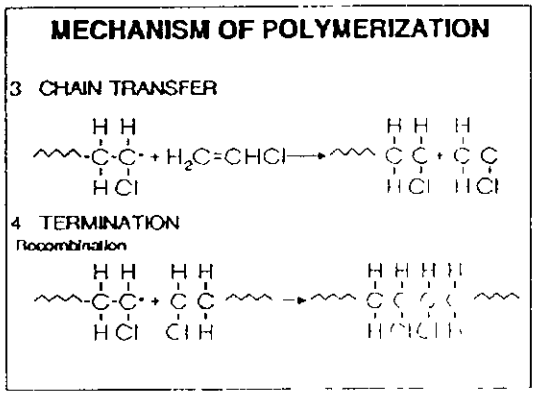
Figure 11. Schematic representation of the formation of suspension PVC

CHEMISTRY

PVC is produced by the polymerization of Vinyl Chloride Monomer (VCM) When a catalyst is added to VCM and brought to run temperature, it produces free radicals that react with vinyl chloride to produce a vinyl chloride radical chain The PVC polymer that is formed is insoluble in the monomer This causes the PVC to separate itself from the monomer as it forms Figure 2 shows a typical building of the PVC Chain







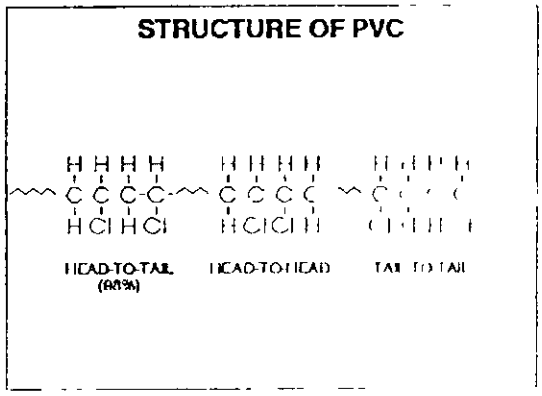


Figure 1-2