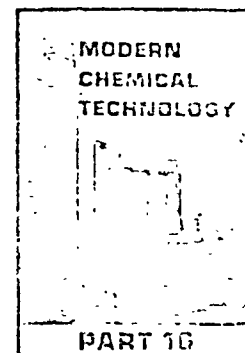


Batch operation of the reactor is the dominant characteristic of almost all commercial processes for making many different varieties of polyvinyl chloride because of the great ease and flexibility in changing recipes from one product to another.



Vinyl Chloride Polymerization by Emulsion, Bulk and Solution Processes

LYLE F. ALERIGHT, *Purdue University*

Emulsion (or dispersion) polymerization is the oldest technique that is used on a large scale for the production of polyvinyl chloride. It was the main process until about 1950 when suspension methods were developed. Recently some of the products produced by emulsion processes have found expanded uses.^{31, 32}

Polyvinyl chloride (PVC) resins produced by emulsion polymerization generally retain all or most of the emulsifier added to the reaction system. About 2 to 5% of the emulsifier is generally present in the polymers. Suspension polymers, however, contain only a relatively small amount of surfactant or stabilizing agent.

In emulsion polymers, the emulsifier is concentrated at the surface of the granular particles that are bead-like and relatively smooth. When plasticizer is mixed with these particles at ambient conditions, it wets them, but the penetration of plasticizer in the PVC beads is slow. Such mixtures of PVC resin and plasticizer form a relatively fluid mixture, assuming that a rather large amount of plasticizer is present in the final material. These are called plastisols. When an organic solvent is also included in the formulation, the liquid mixture is termed an organosol.

Plastisols and organosols are used in dip coatings, slush moldings, rotational moldings and foam applications. In the final steps of the fabrication operation, the temperature is raised to 160 C. for a short period of time. The heat causes total or partial solvation and uniform mixing of the PVC and plasticizer. Upon cooling these mixtures, the plasticizer may be rather uniformly mixed throughout the plastic. In other cases, the final plastic has a PVC-continuous phase, and a plasticizer-discontinuous phase. Such a plastic has

different physical and chemical properties as compared to that containing only a single phase.

Factors Affecting Polymerization

Many recipes are used commercially in emulsion polymerization. The following materials are always present, and the approximate range^{9, 13, 16, 31, 32} at which each is added are:

Vinyl chloride	100 parts by weight
Water	150 to 250 parts by weight
Soap or surfactant	2.0 to 5.0 parts by weight
Water-soluble initiator	0.1 to 0.4 parts by weight

For an outline of the mechanism of emulsion polymerization, see the summary on the next page. Additional details were given in an earlier article.¹

In the emulsion polymerization process, only highly purified vinyl chloride should be used. In addition, deionized and deaerated water is required.

A wide variety of soaps or surfactants are used including sodium lauryl sulfate, other sulfated esters, ammonium stearate, sulfonated castor oil, sulfonated higher alkyl alcohols, alkyl naphthalene sulfonic acids, other types of synthetic detergents, and just plain soaps (salts of lauric, myristic, palmitic, and stearic acids). In addition, nonionic emulsifiers are sometimes used, especially to make polymers for electrical applications.

Hopf and Fakla¹⁸ investigated the relationship between the chemical nature of the emulsifiers and rate of polymerization, and the properties of the resulting PVC. Sodium salts of the sulfuric acid esters of fatty alcohols, having 10 to 18 carbon atoms, gave PVC polymers with the highest molecular weights. Paraffin sulfonates, sulfates, and salts of fatty acids

To meet the author, see *Chem. Eng.*, Feb. 13, 1967, p. 164.

had similar effects relative to polymerization. Unsaturated emulsifiers decrease the rate of polymerization. Nonionic emulsifiers were less active than the anionic variety. In general, the effect of emulsifiers on the polymerization reaction decreases as the molecular weight of the emulsifier increases.

PVC resins for electrical applications such as wire coatings must be prepared by using nonionic emulsifiers or decomposable emulsifiers. The latter are quite stable during polymerization, but they can be saponified later.²² Residues of the emulsifier are removed by washing the granular PVC product. Some emulsifiers in this category include: hydroxylated olefin and fatty acid esters, sulfonic acid esters, and phosphonic acid esters.

Initiators Are Water Soluble

Some of the more important water-soluble initiators are: ammonium persulfate, potassium persulfate, hydrogen peroxide, and various redox systems such as chlorate-bisulfite combinations. The initiators are soluble to some extent in the vinyl chloride phase. As a result, a small amount of an essentially suspension-type polymerization may occur in that phase. Peggion and others²³ indicate that the polymerization rate is proportional to the 0.6 to 0.7 power of the initiator concentration; whereas Smith and Ewart²⁴ predict that it should be proportional to the 0.4 power. Al-

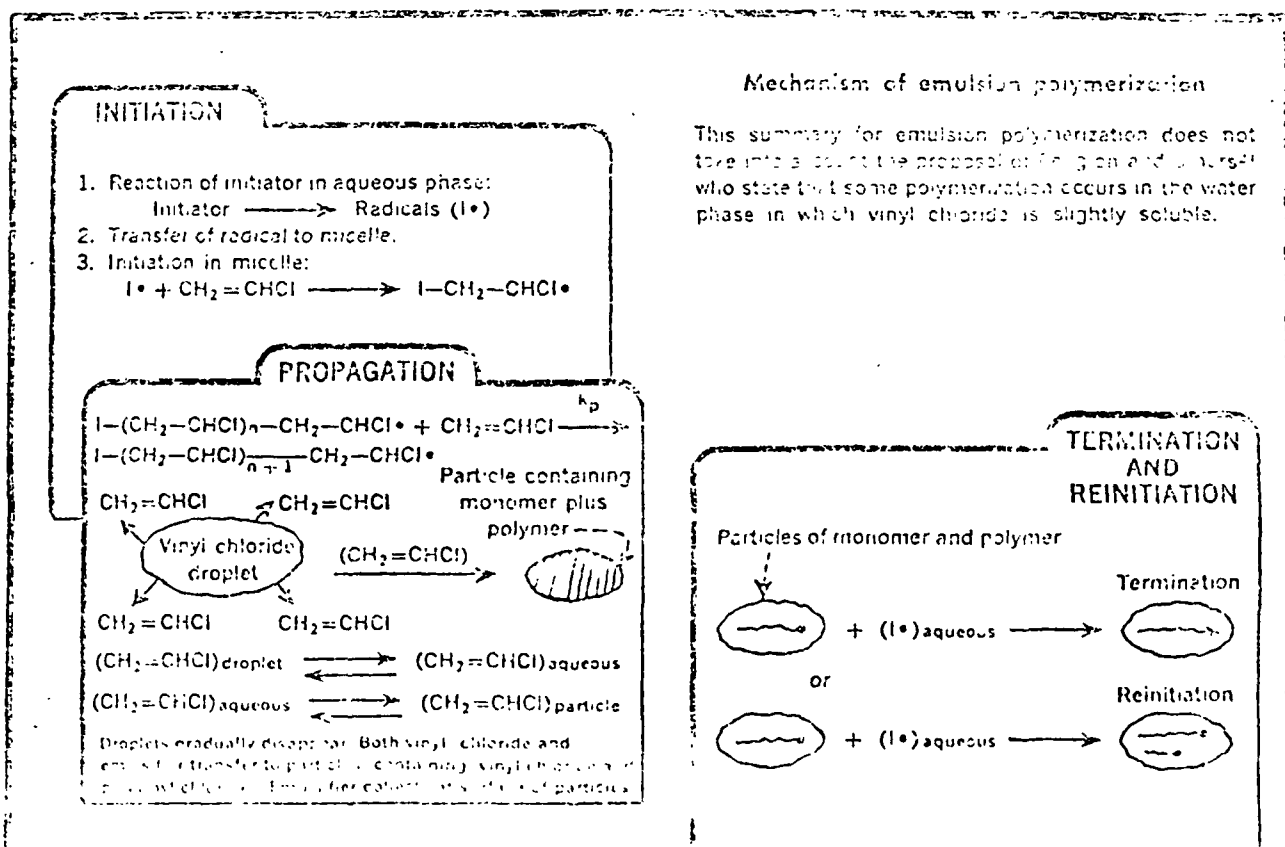
though several investigations²⁵⁻²⁷ present valuable kinetic information concerning emulsion polymerization, much additional information is needed.

Relatively little quantitative information is available in the literature regarding temperature. Apparently temperatures used commercially vary from about 30 to 55 C. Higher temperatures are not generally used (as in the suspension process) because the PVC would have a relatively low molecular weight and consequently would be relatively thermally unstable. Temperature would affect not only the rate of decomposition of the initiator and other chemical reactions, but also the nature of the emulsion and transfer of reactant to the growing polymer particle.

Batch Processes for Emulsion Polymerization

In the U.S., batch processes are used predominantly if not exclusively as compared to continuous-flow processes that are or have been used in Europe. Batch processes have two important advantages:

1. Increased ease of producing a large number of distinct types of PVC resins without producing significant quantities of off-specification product. In a continuous-flow process, there is always the possibility of producing relatively poor quality materials especially during start-up or while switching from one product to another.
2. Better control of operating variables during



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polymerization and, hence, better control of quality in the final polymer. Difficulty is probably still experienced in obtaining the highest quality PVC resins in continuous-flow processes.

Much of the equipment used for emulsion polymerization is the same as that used for suspension polymerization. In the Firestone plant, the only major equipment difference seems to be in the drying operation.¹ Since much of the equipment is used interchangeably, the operating steps are also very similar.

Details of the method of seeding reactions in the autoclave are not known. Presumably there are several commercial variations. First, the emulsifier, initiator, and possibly a buffer are dissolved in deionized water. Relatively cool water is normally used because the initiator begins to decompose as soon as the temperature is raised. The water solution is added to the autoclave, and care is taken to exclude air (or oxygen) from the system. The desired amount of vinyl chloride is added, and agitation is started to form a relatively stable emulsion.

When the emulsion is heated, the reaction begins. Temperature control is often critical during the most rapid phase of polymerization. Adequate temperature control is maintained by cold brine or water in the jacket. Baum⁴ outlines some of the method for increasing the over-all heat-transfer coefficients:

- a. Introducing the brine through nozzles to produce tangential, high-velocity swirling brine or water.

- b. Baffled design for the jacket. Proper installation is relatively expensive, and this method is apparently not too widely used.

- c. Rapid convection or pumping of brine through the jacket.

When possible, cold vinyl chloride is added to the polymerization vessel in order to moderate the temperature. Baum⁴ indicates that a reflux condenser is sometimes used in some types of emulsion polymerization. As indicated earlier,¹ such a technique is probably not applicable for producing PVC resins.

Often 90 to 95% of the vinyl chloride is polymerized in each batch run. The rates of polymerization decrease rapidly at higher conversions, and reaction time is 12 to 18 hr. Pressure decreases as the run nears completion.

Recovery of PVC Particles

Separation of unreacted vinyl chloride from the emulsion and its subsequent recovery, purification, and recycling involves the same equipment as used in the suspension process. The remaining emulsion or latex is stored in blend tanks until several batches are collected. The most popular method for recovering solid PVC particles is by spray drying because it is relatively difficult to separate the emulsion by centrifuging or filtering. Rivsavy¹⁰ has indicated some of the factors of importance regarding spray drying, and Labine¹¹ describes the spray drying of PVC latex. Drum dryers have also been used. Sometimes, the emulsion is coagulated, separated by filtration or centrifugation, and dried in a vacuum oven. The dried PVC product

is collected, classified, and stored until packaged in silos having capacities of 100,000 to 200,000 lb.

Modified Emulsion Polymerization

In a conventional emulsion polymerization, initiation occurs in the micelles; but in some modified methods, few if any micelles are present. Rather the conventional initiation of polymer particles is bypassed. Instead, the reactor is seeded with tiny polymer particles. Polymerization then proceeds in the conventional manner, namely polymerization occurs on or in the latex (or seed) particles. Several modifications of seeding are probably used, but the patented process by Powers¹² is an important method.

Powers explains the relationship between PVC particle size and the amount of dispersing agent (such as soap) necessary to maintain a stable emulsion, that is the prevention of coalescence of the PVC particles, or formation of additional dispersed particles in the emulsion. The area A covered to a thickness of one molecular layer by a mole of dispersing agent is:

$$A = N_A A_o \quad (1)$$

where N_A is Avogadro's number, and A_o is the cross-sectional area for a molecule of the dispersing agent. Such values are often available in handbooks.

Since the individual PVC particles are essentially spherical in shape, the weight W for the dispersing agent of molecular weight M required to cover the surface of a particle of diameter d is:

$$W = \pi d^2 M / N_A A_o \quad (2)$$

The weight W_p of polymer with density ρ in each particle is as follows:

$$W_p = \pi d^3 \rho / 6 \quad (3)$$

Then the weight percentage P of the dispersing agent (based on the weight of the polymer) that is needed to cover the surface of a particle is obtained by dividing Eq. (2) by Eq. (3), and then multiplying by 100:

$$P = \frac{W}{W_p} \times 100 = \frac{600M}{N_A A_o \rho d} \quad (4)$$

Of course, the particles in an emulsion have a range of diameters. The surface area is proportional to the diameter squared, whereas the volume is proportional to the diameter cubed. In general, the diameters of the particles present in an emulsion follow a normal probability distribution. Corrections must then be made to Eq. (2), (3) and (4) when P is calculated. A semitheoretical correction technique has been presented by Powers.¹² He reports that when the weight percentage P of 20 to 60% (preferably 25 to 40%) is used, significant coalescence and formation of particles do not occur.

The actual fraction of P that is required is undoubtedly to some extent a function of temperature, amounts of reactants and other additives, and degree of agitation. By implication, Powers apparently believes that 25 to 40% of P is a good value for the usual range of operating conditions in emulsion polymerization processes.

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In the Powers' process, additional vinyl chloride and dispersing agent are added during the course of the batch reaction. The additional vinyl chloride provides more monomer for polymerization, and the additional dispersing agent maintains a stable emulsion as the PVC particles grow. The vinyl chloride undoubtedly would be added cold because it would control reactor temperature. Hence, a higher rate of polymerization is possible.

In an example of the Powers' process, the final PVC latex was to have an average diameter of 2,530 Å. Sodium stearate was the dispersing agent. The following charge was added at the start of a batch run in a 15-gal. reaction vessel:

Vinyl chloride	9.0	lb.
Water	36.7	lb.
Potassium persulfate	0.27	lb.
Ammonium hydroxide (28% solution)	0.27	lb.
Seed latex	0.80	lb.
Sodium stearate	0.013	lb.

The seed latex contained PVC particles with an average diameter of 342 Å. Table I indicates how the vinyl chloride and dispersing agent were added during the run, and the formation of polymer.

The dispersing agent was added in a 5% water solution. The solution had to be added more rapidly at the beginning of the run than at the end. Vinyl chloride was added at an approximate rate of 2.4 lb. hr. for the first 10 hr. of the run, and at about 3.2 lb. hr. for the next 6 hr. The rate of vinyl chloride addition was decreased for the next 4 hr. and finally stopped at the end of 20 hr. The latex particle produced at the end of the run (23.2 hr. and 95% conversion) had an average size particle of 2,530 Å, essentially that predicated in the patent.¹²

Adding both the vinyl chloride and the dispersing agent at a variable rate during the batch run is a complicating factor. Hence variable-speed or variable-flow pumps or feeding devices are required. Several analyses of the emulsion during the run are probably done in order to check the course of the polymeriza-

tion. Highly trained operators are needed to ensure high quality PVC.

Polymer formation lags behind the amount of vinyl chloride added to the reactor by 1 to 13 hr., as shown in Table I. The largest lag occurred at about 16 hr. In the range from 16 to 23 hr., rate of polymerization was most rapid, except possibly for the rate during the first hour. It would seem as if an auto-acceleration reaction is occurring during these periods.

Using the Powers' process, PVC particles varying in size from 500 to 20,000 Å. can be produced because the emulsions formed in this range are highly stable. Latexes in which the PVC particles are as small as 100 to 200 Å. can be used for seeding, but these emulsions are quite unstable and must be used within a few hours. If the seed latexes have somewhat bigger particles, they will be stable for longer periods, up to several days or even weeks.

The volume percent of PVC particles that can be stabilized in an emulsion varies up to about 65%. In most commercial applications, the volume percent is probably reasonably high in order to minimize the problems of removing water from the polymer.

This modified emulsion technique has important advantages as compared to regular emulsion processes. Particle size can be better controlled. Furthermore, larger particle size can be produced uniformly. In addition, the amount of dispersing agent can be minimized because it is added only as needed to stabilize the particles. In the above example, the final PVC polymer contains about 1.6% emulsifying agent. This is considerably less than that for most conventional emulsion polymers. An even smaller quantity would be present if larger PVC particles were produced. The modified method of emulsion polymerization is related to suspension polymerization in that only polymer-monomer particles occur in the dispersed phase of the water.

The method of preparing the seed polymer is not known. Presumably it would be prepared in a relatively small reactor.

Example of a batch run for a seeded emulsion-polymerization process—Table I

Time Hr.	Total Vinyl Chloride Added To Reactor Lb.	Total Dispersing Agent Added To Reactor Lb.	Theoretical Amount Of Dispersing Agent In Reactor %	Amount of Polyvinyl Chloride In Reactor Lb.
0	9.0	0.013	35	0.15
1	14.4	0.164	22	4.2
2	14.4	0.164	30	8.7
4	18.9	0.20	26	14.1
6	23.2	0.21	23	18.0
8	27.8	0.37	35	22.8
10	33.3	0.37	32	26.4
16	52.4	0.53	35	39.6
20	60.0	0.60	34	49.1
23.2	60.0	0.60	31	57.0

Data for Table I were obtained from the patent.¹²

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Continuous-Flow Emulsion Polymerization

Descriptions of relatively old German processes have been given by Dunlop and Reese,¹² Delorme,¹³ Herte,¹⁴ and Krehler and Wicker.¹⁵ The reactor vessels have a relatively large height-to-diameter ratio. One vessel is described as being 23 ft. tall, about 5.4 ft. diameter, and having a capacity of 3,600 gal.¹² It is glass-lined and is jacketed for cooling as desired with brine or cold water. A simple-blade or paddle agitator is provided near the top of the vessel. This paddle was specified as being 4 ft. diameter and 1.5 ft. high. A variable-speed motor is used to turn the agitator at speeds up to 50 rpm.

Water (containing the dissolved emulsifier, initiator and buffer) is fed continuously to the top of the reactor through one feed line, and vinyl chloride is metered to the reactor through another. A maximum degree of shear is apparently needed in the emulsion near the feed point; But Dunlop and Reese¹² characterize it as "gentle swirling," which implies relatively low speed. They further indicate that the level of agitation is most important. Of course, relatively little agitation is provided in the bottom of the reactor. As PVC particles form, they become heavier than the vinyl chloride droplets in the emulsion because of the greater density of PVC as compared to vinyl chloride. It is doubtful that any significant phase separation occurs in the bottom of the reactor because the emulsions normally formed are very stable.

Variations in the arrangement of reactors occurred in German plants. In one, multiple reactors were arranged in parallel-flow.¹⁷ In another, the relatively large reactor (previously described) was connected in series with a much smaller unit.¹² In the latter, about 88% polymerization of the entering vinyl chloride occurred in the first (and larger) reactor, and an additional 4% reacted in the second. The theoretical residence time of vinyl chloride in the two reactors was 28 hr. Blue dye injected in the feed stream did not appear in the exit stream for 20 hr. Hence a small amount of back mixing was occurring, but the flow in the bottom portions of the reactors must have been essentially plug flow. The blue color persisted in the exit stream for 100 hr.

Temperature was reported as the controlling factor relative to the capacity of the reaction system. Depending on the specific polymer desired, these temperatures vary from 38 to 50 C. Uniform temperatures are desired throughout the reactor, but with the laminar flows that undoubtedly occur in the bottom of the reactor, the over-all heat-transfer coefficients tend to be low. Some convection currents occur because of temperature gradients in the emulsion from the heat of polymerization.

Operators of the German plants indicated that a delicate temperature balance occurred. Increased initiator concentrations raise the reaction temperature and rate of reaction. The temperature of the brine or water in the jacket is also important relative to temperature control.

Start-up of the reactor required several hours in

order to minimize production of off-grade polymer. The reactor was filled with cool water, emulsifier solution, initiator and vinyl chloride.¹² Warm water was used in the jacket of the reactor until the reaction mixture was sufficiently heated to start polymerization. Gradually, cooling water was substituted in the jacket, and the density of the emulsion was measured frequently until it reached the desired level. At this time, the continuous flows of vinyl chloride and water solution were started. Start-up was then considered to be completed.

When multiple reactors are arranged in series, the number of feed pumps, feed lines, etc., would be minimized. Furthermore, temperature control would be easier. Although the reasons for using reactors arranged with parallel-feed systems are not specified, such a flow arrangement would allow much greater flexibility in producing various types of PVC resins.

Processing of the emulsified product from the reactor was similar to that in batch processes except a continuous-flow system could be used.

Process improvements have no doubt been made in the continuous-flow processes described here. Unfortunately details are not available.

Bulk Polymerization

Bulk polymerization of vinyl chloride has established itself as an important process within the last few years.⁶⁻¹⁶ Announced world capacity for the Pechiney-St. Gobain two-step process is 600-million lb. yr. of PVC. Two American companies are presumably planning to use this process. Important advantages of this process are:

1. The final polymer contains no impurities such as emulsifying agents or surfactants.
2. The polymerization process is likely or potentially cheaper than other processes because there are no inert materials such as water or solvents that must be separated from the final polymer.

Quality of the polymer obtained by this process is claimed to be at least as good as that of the best suspension-type PVC.

Two recipes²⁶ for bulk polymerization are:

	Recipe 1	Recipe 2
	Parts by Weight	
Vinyl chloride	100	100
Azo-bis-isobutyronitrile	0.016	0.02
Diisopropyl percarbonate	—	0.00005

Two-Step Bulk Process

In the Pechiney-St. Gobain process, two reactors operated batchwise and in series are used commercially.²⁷ In the first reactor, approximately 10% of the vinyl chloride is polymerized. Polymerization continues in the second reactor until a total of 75 to 80% is polymerized. The remaining 20 to 25% of the vinyl chloride is vaporized, recovered and recycled.

The first reactor is a vertical one. It is provided with very fast agitation.²⁷ It is the only one designated as a prepolymerizer. Details on this reactor

and the phenomena occurring in it are not known. However, several investigators^{1-5,22} who have conducted mass polymerizations of vinyl chloride have reported considerable information about this phase of the polymerization. A precipitate of PVC particles is first noted when about 4 to 8% of the vinyl chloride has polymerized. The exact conditions at which precipitation starts depends on various operating effects including temperature. Rather surprisingly coagulation of the PVC particles is shifted to higher conversions as the temperature is decreased,²³ but perhaps viscosity plays a role in the rate of coagulation.

The precipitate of PVC solvates considerable amounts of vinyl chloride—perhaps 5 to 6 parts of vinyl chloride per part of PVC polymer. At about 15 to 20% polymerization, the liquid phase of vinyl chloride essentially disappears. Hence when a 10% polymerization has occurred, probably over half of the original liquid phase has disappeared, i.e., it has either polymerized or been solvated. Temperature control up to 10% reaction is possible by heat transfer through the reactor walls. Sufficient vinyl chloride liquid is available to provide relatively high heat-transfer coefficients.

High rates of agitation are needed for two reasons: (1) formation of particles with rather uniform sizes. Sizes from 100 to 200 microns, or even larger,¹⁸ are possible. With proper operating conditions, the particles can be quite porous and have low bulk densities. The agitation, of course, affects the complicated phenomena of dispersion followed by agglomeration of the particles; (2) promotes good heat transfer with the cooled walls of the prepolymerizer.

About 10% polymerization of vinyl chloride is achieved in the prepolymerizer after about 3 hr.²⁴ The exact time depends on the temperature (probably 50 to 60 C.), and the amount of initiator.

Operation of Second Reactor

The second reactor, or autoclave, is stirred with ribbon blenders. These horizontal autoclaves are reported to have volumes of approximately 424 cu. ft.^{6, 19} Based on published pictures, each autoclave appears to be about 5-ft.-dia. and 20 ft. long. Details of the ribbon blenders are not known, but a patented version has two or three ribbons wound on whorls of different diameters.⁸ One of the ribbons turns in an opposite direction to the others. The autoclave blades are continuously cleaned by the stirrer blades, and good heat exchange is maintained.²⁵

Operation of the second reactor is the critical portion of this process. Undesired agglomeration of the PVC particles must be prevented, and adequate temperature control must be maintained as the reaction mixture is transformed from a slurry, through a sticky solid stage, to essentially dry particles. The speed of the ribbon blenders is decreased as polymerization progresses from perhaps 20 to 30 rpm. to 5 to 10 rpm.¹⁹ The second portion of the reaction probably requires 10 to 15 hr. in order to obtain the desired polymerization.¹⁶

The autoclaves are jacketed, and water or brine is used as coolant.⁶ Part of the heat of reaction is removed by the vaporization of 20 to 25% of the original vinyl chloride feed. A reflux condenser can possibly be used to control the reaction temperature, assuming that excessive polymerization does not occur on the condenser surfaces.

Materials of construction for the commercial autoclave are not specified, but a stainless steel one was used in the examples given in the patent.²⁶ By implication, perhaps the problems of polymer formation on the reactor walls are quite different than those in suspension polymerization where glass-lined reactors are required. Additional information is necessary relative to what surfaces and operating conditions promote "polymer skins" in bulk polymerization. The temperature used commercially in this reactor is not reported, but is likely in the range from 50 to 60 C.

Presumably the autoclave is operated only partly filled in order to obtain adequate blending. Perhaps it would be 50% filled, which would mean 210 cu. ft. of material. Bulk densities of PVC product are about 0.3 g./cc., or higher. Hence, PVC product per batch will be 4,000 lb., or greater, and 5,000 lb./batch might be an average value. A total of 500 to 600 batches/yr. is probable because time must be allowed for cleaning and maintenance. Average annual capacity of each autoclave is then estimated to be 2.5 to 3.0-million lb.

The prepolymerizer vessel, however, can be essentially filled for each batch. It should be large enough to handle a batch for the autoclave, which might be as high as 6,000 lb. Since some vinyl chloride is vaporized during polymerization, up to 8,000 lb. of vinyl chloride may be added to the prepolymerizer. This vessel should then be capable of holding about 140 cu. ft. of liquid; and for the vessel described, a capacity of 160 to 180 cu. ft. would presumably be adequate for this vessel.

Attempts have been made to perform both prepolymerization and final polymerization in the same vessel. In one case,²⁶ the initial prepolymerization was conducted by using a very high rate of agitation. Less vigorous agitation and a different agitator were used for the later stages of polymerization. Probably this method is not used commercially, and it would have the major disadvantage that a large vessel would be needed for both stages; whereas a smaller vessel is adequate for prepolymerization in the two-stage process. In the conventional process, a prepolymerizer vessel can probably service at least two and possibly three autoclaves.

Cost Data for Process

The flowsheet for the entire process has been reported by Krause.¹⁹ Recent patents^{7, 8, 20, 28} probably explain some of the specific details. Recovery, purification and recycle of unreacted vinyl chloride appears much simpler than in suspension-type processes. The PVC product requires little additional processing. Probably the cost of polymerization by this method would be considerably less than by suspension methods, perhaps about 2¢/lb. of PVC formed as compared to 3¢

by the suspension process. In addition, investment costs are claimed to be less.¹² A 48-million lb./yr. plant is reported to cost \$1.7 million, excluding storage tanks and packaging.

Solution Polymerization

Solution polymerization, as practiced in most commercial processes, is not a true solution polymerization since polymer precipitates from the solution. The term "precipitation" polymerization is sometimes applied to this type. In several respects, this polymerization is related to bulk polymerization because the polymers are quite insoluble in the liquid phase.

In bulk polymerization, the polymer begins to precipitate from the liquid phase when about 8 to 10% of the vinyl chloride has polymerized. In solution polymerization, the solubility of the polymers in the mixture of solvent and vinyl chloride depends on the solvent, the concentration of vinyl chloride in the solution, and composition and molecular weight of the polymer and copolymer.²⁴ When cyclohexane is the solvent, a granular precipitate occurs from the "start" of the run. Tetrahydrofuran is a "good" solvent for PVC polymer, and precipitation does not immediately occur. Temperature control is easier to obtain for solution (or precipitate) polymerization as compared to bulk polymerization because the large amount of solvent acts as a heat sink.

When polymer begins to precipitate from solution, auto-acceleration is frequently noted because the precipitate contains considerable amounts of solvated vinyl chloride (and possibly comonomer) in addition to polymer or copolymer. The polymerization reaction continues in the precipitate, and the polymer so produced has a much higher molecular weight than that produced in solution. This latter polymer tends to have relatively low molecular weight because of chain-transfer reactions with the solvent. A thorough discussion of the complex mechanism of solution (and precipitation) polymerization is given by Mickley, Michaels and Moore.²⁵

The basic process that Union Carbide Corp. is thought to be using is probably described in two patents.^{11, 26} Presumably the process is used to make copolymers containing 75 to 90% vinyl chloride, with the remainder being vinyl acetate. The mechanically-stirred autoclave maintained at approximately 40 C. contains a slurry consisting of about 80% solvent, designated as *n*-butane. The remaining 20% consists of the comonomers dissolved in the solvent, and solid copolymer present as a precipitate. The slurry is pumped to a filter press to remove the precipitate, and filtrate is returned to the autoclave. Make-up comonomers and initiator are continuously added to the autoclave.

The process as described in the 1933 and 1937 patents has undoubtedly been modified as newer equipment has become available. Two batch filter presses were originally specified. One filter press was emptied and cleaned while the other was being used. Such filters would have two disadvantages:

1. Considerable hand labor.

2. Possibility of air leaking into the system because the filter presses are opened and exposed to air during the cleaning cycle.

Either centrifugal separators or continuous-flow filters are probably used in modern commercial processes.

Lead-lined autoclaves were specified in the patents, but glass-lined reactors are likely used now. The lead was probably used as a corrosion-resistant material and not as a catalyst.

Benzoyl peroxide was specified as the initiator at concentrations of about 0.5% by weight. Popular initiators such as lauroyl peroxide and isopropyl peroxide would likely be satisfactory in present commercial processes. Azo-bis-isobutyronitrile was used in the recent experimental program of the precipitation polymerization of vinyl chloride.²³

The separated solid polymer or copolymer particles contain considerable amounts of dissolved vinyl chloride and some solvent.²³ Polymerization reactions will continue until the vinyl chloride is separated from the solid particles. Temperature and pressure to which the separated particles are subjected is most important relative to flashing of the vinyl chloride from the particles of solid product.

Solvents, other than *n*-butane, have been used in experimental investigations,^{14, 20} and include the following: benzene, chlorinated aliphatics, cyclohexane and tetrahydrofuran. Normal paraffins such as *n*-butane contain only primary and secondary carbon atoms, and they are less active as chain-transfer agents than isoparaffins such as isobutane that contain a tertiary carbon atom.

An important advantage of solvent polymerization is that water is not used. Hence, recovery of the final product is simplified. The unreacted vinyl chloride and solvent are generally easy to remove, especially if a relatively volatile solvent such as *n*-butane is present. The recovered vinyl chloride and solvent are probably recirculated as a mixture. The final polymer product contains few impurities since presumably no emulsifiers or surfactants were present. However, the products probably tend to have relatively low molecular weights because all solvents act to some extent as chain-transfer agents.

Low-Temperature Solvent Polymerization

Solvent polymerization of vinyl chloride has recently been publicized as at least one of the techniques for producing an improved polyvinyl chloride that is being used in making 100% PVC fibers.²⁶ Several American companies are thought to be interested in these newer types of PVC fibers. In France, PVC fibers have captured the following shares of the market: flags, 60%; curtains, 35%; underwear, 30%; ski and mountain clothing, 25%; sweaters and blankets, 20%; and auto and airplane interiors, yarns, and artificial furs, 10%. These PVC fibers are significantly cheaper than nylon, polyesters and acrylic fibers.

New processes have been developed to obtain PVC fibers with improved properties. Low-temperature

polymerization techniques are generally used with a suitable catalyst and solvent. Societe Rhovyl¹² is thought to be polymerizing vinyl chloride at temperatures from -10 to -20 C., and Applicazioni Chimiche Societa per Azioni¹⁶ polymerizes at -20 to -60 C. by using a mass-polymerization technique. The resulting polymers are more highly syndiotactic because of the low polymerization temperatures, and they are quite resistant to boiling water and to dry-cleaning solvents.

Societe Rhovyl indicates that fibers can be produced with break strengths of greater than 2g./denier, shrinkage in boiling water of less than 10%, and shrinkage in trichloroethylene at 40 C. of less than 10%.¹⁵ Actual shrinkage values are probably significantly less than 10%. Adhesive fibers can be prepared if a copolymer of vinyl chloride and vinyl acetate is produced or dissolved in various water-soluble solvents before spinning.³⁴ Suitable solvents include acetone, tetrahydrofuran, dimethyl formamide (DMF), and dimethyl acetamide (DMA).

Copolymerization by a solvent-polymerization technique must lead to interesting mass-transfer features. The relative rates of transfer of the comonomers from the solvent phase to the solid copolymer particle are likely quite different. If so, the composition of the copolymer would presumably change as the extent of polymerization varies.

Chlorination of PVC Resins

High-temperature stability of PVC polymers regardless of the method used for polymerization can be improved by chlorination. Chlorine adds to the unsaturated and relatively unstable end-groups of the polymer molecules. As a result, zipper dehydrochlorination is significantly suppressed.

Chlorination of PVC resins is used to a limited extent, but the commercial method for this chlorination is not known. The PVC resin could be dissolved in a suitable solvent, and the the solution could be contacted, at the proper conditions, with chlorine. This technique would appear to be expensive since PVC resins are only slightly soluble in most common solvents. Large quantities of solvent would appear to be necessary, and the cost of evaporation and crystallization would likely be high.

Another possible technique would be to use a fluidized-bed in which a gas, containing chlorine, was contacted with granular PVC resins. Chlorination would initially occur on the surface of the solid particles. Chlorine molecules would presumably slowly penetrate to the interior of each particle. Possibly some substitutive chlorination would occur especially on the surface of the particles.

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Key Concepts for This Article

Active (8)	Passive (9)	Means/Methods (10)
Manufacture*	Polyvinyl chloride*	Processes*
	Copolymers*	Polymerization*
	Plastics*	Emulsions*
	Polymers*	Solutions (mixtures)*
		Bulk*

(Words in bold are role indicators; numbers correspond to EIC/ACM system except for Role & modification. Asterisks indicate concept suggested for indexing; others are added to improve readability as an abstract. Indexing is described in *Chem. Eng. Prog.*, 61, 1165, p. 187, or you may order Key Concept report, 50¢, using Reader Service Postcard.)