
**Introduction**

Polyvinyl chloride (PVC) commercial development began in the early 1930s, when it was discovered that heating the brittle PVC with plasticizers gave a flexible material functionally equivalent to rubber. Unmodified PVC resin has very little utility due to poor physical properties and processability. PVC is almost always converted into a compound by the incorporation of additives such as plasticizers, heat stabilizers, light stabilizers, lubricants, processing aids, impact modifiers, fillers, flame retardants/smoke suppressors, and, optionally, pigments. A typical rigid PVC compound can have total additives of 8 to 37 parts per 100 parts of base resin (phr). In addition, flexible PVC compounds can contain 25 to 80 phr of plasticizer. The use of plasticizers sometimes requires the use of biocides to inhibit microbiological attack that may result in discoloration or loss of properties.

PVC has proven to be an extremely versatile material, and is used in both rigid and flexible forms. Rigid PVC applications include pipe and fittings largely for water service (supply and drainage); profiles for windows, doors, and siding; film and sheet for packaging and construction uses; and blow molded containers for household and health and beauty products. Flexible PVC, in compounds characterized by a high loading of plasticizers, is used in a variety of applications including film and sheet for packaging, coated fabrics for upholstery and wall coverings, floor coverings for institutional and home use (bathrooms and kitchens), tubing for medical and food/drink uses, and wire and cable insulation.

PVC can be fabricated into useful end products by a number of techniques, including extrusion, calendering, injection molding, blow molding, and coating. The largest amount of PVC is processed by extrusion to give pipe, siding and window/door profiles, wire and cable insulation, and rigid film/sheet. Calendering is used in processing flexible film/sheet for upholstery and wallpaper. Injection molding is used primarily for pipe fittings and automotive/appliance parts. Coating of various substrates provides an impervious protective layer. PVC coated fabrics are used in protective clothing including outerwear, aprons, and gloves.

**Chemistry**

PVC process chemistry comprises four principal steps:

- Initiation
- Reactive monomer radical propagation
- Chain transfer
- Chain termination

The polymerization reaction begins when the initiator decomposes to form two free radicals for each molecule of initiator. An initiator fragment adds to a molecule of vinyl chloride monomer. The electrovalent imbalance results in the formation of a reactive monomer radical.

The reactive monomer radicals are then free to combine with other vinyl chloride molecules and the polymer chains begin to form. Chain transfer also occurs, but it is detrimental only in that it slows the rate of increase of the molecular weight of the chain.

Termination of the reaction is achieved by introducing a chain stopper such as butadiene. This reduces the concentration of free radicals by either coupling or disproportionation. Coupling results in the combination of two chains to form one chain with a molecular weight equal to the sum of the original two.

In disproportionation, however, the two chains do not combine, but exchange a hydrogen ion to achieve a nonreactive state in which one chain is saturated while the other has a double bonded vinyl group at its “tail”.

The stereochemistry of the chain is a function of reaction temperature. The degree of syndiotacticity (i.e. the extent to which the chlorine atoms alternate from one side of the chain to the other) ranges from 55 percent at 55°C and higher to 68 percent at -76°C. All commercial processes are run in the range 55°C to 70°C reaction temperature (i.e. the lower end of the syndiotactic scale).

The polymerization reaction can leave the polymer chain with a variety of weaknesses, most commonly unsaturated double bonds at around 2 per 1,000 monomer units. Additional problems that can lower the basic thermal stability of the chain are head to head units and labile chlorine atoms. These molecular structure defects act as potential sites for chain fracture either by thermal or photochemical action.

**Production Processes**

The major technique of polymerizing vinyl chloride monomer (VCM) to PVC is by suspension polymerization carried out in small droplets of monomer suspended in water. VCM is dispersed in water by agitation, and the droplets are stabilized by the action of a suspending agent such as a protective colloid (often polyvinyl alcohol). The activation for polymerization comes from monomer soluble initiators that generate free radicals upon thermal decomposition. Other additives are also used, such as chain transfer agents, which together with the polymerization temperature, determine the polymer chain length and hence molecular weight. Antifoams suppress foaming in various process steps. Build-up suppressants minimize polymer build-up on equipment surfaces.
The physical structure of the PVC granule is determined during polymerization. It later affects the rates at which residual VCM can be removed, plasticizers and other additives can be absorbed, and gelation (melting or fluxing) can be achieved (in the fabricating machinery).

The typical size of PVC suspension reactors is in the range of 60 to 90 cubic meters, with some as large as 200 cubic meters. Several design problems had to be resolved before large reactors could be operated successfully. The problem of heat removal from the polymerization reactor is compounded as reactor volume increases, because the ratio of surface area to reactor volume decreases but the heat removal requirements increase linearly with reaction volume. In suspension polymerization, obtaining the proper resin particle characteristics hinges on maintaining good monomer suspension throughout the reactor vessel, becoming more difficult in larger vessels.

The heat removal problem was solved in several ways. The use of stainless steel (instead of glass lining) was made possible by the development of antistick agents. Mild steel reactors clad with stainless steel offer significantly higher heat transfer coefficients than glass-lined or solid stainless steel reactors. The use of co-initiator systems has resulted in a nearly constant rate of heat evolution, which translates into larger permissible capacity for a given reactor configuration.

An external reflux condenser can be employed to boost heat removal capability. Condenser plugging is mitigated by coating it with the same antifouling agents used for reactor vessels. If a reflux condenser is used, antifoaming agents are added to the reactants to prevent foam containing initiators from reaching the condenser. Water cooled baffles are another means of increasing heat transfer area.

The problem of maintaining proper suspension in larger reactors with length-to-diameter ratios of about 2:1 has led to the use of bottom drive agitators. The bottom-drive agitators have shorter, thinner shafts than top mounted agitators.

The suspension process is a batch operation as far as polymerization is concerned. The finishing section is operated continuously with several reactors operating on the same grade, discharging in sequence into a buffer tank.

During the polymerization reaction pressure remains constant until 70 to 75 percent of the monomer has been converted. From this point on, the pressure begins to decrease, since the free monomer has been converted and the remaining monomer is absorbed in the polymer, which reduces the monomer partial pressure. This is illustrated in Figure 1, where a typical batch cycle is seen to be about 6.5 hours. The pressure is usually allowed to drop 3 or 4 bar (40 to 60 psia), which corresponds to a monomer conversion of approximately 90 percent. At this point, the reactor contents are depressurized into the slurry stripper feed tank, where most of the unconverted monomer vaporizes. The vapor stream evolved is directed to the monomer recovery system. The depressurized slurry leaves the slurry stripper feed tank and is pumped to the top of the slurry stripper. At this point, the slurry typically contains 10,000 ppm vinyl chloride.
Ease of removal of VCM depends on PVC particle size, particle size distribution, presence of “glassy” particles, and particle porosity. Thus, proper stripping conditions have to be determined for the various PVC grades.

Most companies now use a slurry stripping tower. The stripper is equipped with perforated plates. Steam enters the column from the bottom while the PVC slurry enters the column near the top. The VCM is stripped from the slurry countercurrently on the various plates of the stripper. Between 1 and 3 percent of the total VCM charge is recovered by the stripper. Thus, the operation is not only indispensable for ecological reasons but also has economic importance. Residence times of the slurry in the stripper should be up to about 10 min.

Stripped suspension slurries typically contain less than 10 ppm vinyl chloride. The PVC slurry exiting the bottom of the slurry stripper is pumped to the polymer drying and solids handling system. The overheads stream from the slurry stripper is sent to the waste water stripping facility while the VCM vapor is drawn to the monomer recovery system by vacuum.

The stripped PVC slurry, containing about 32 percent PVC solids, is sent to a dewatering centrifuge, that discharges a resin cake with a moisture content of about 21 percent. The liquor from the centrifuge is stripped of VCM before being discharged to waste.
The PVC granular solid is dried in air and the residual VCM content reduced to 1 ppm. This is done either by a fluidized bed or rotary drum dryer. PVC storage is provided in a bulk storage silo. From there, resin is transported to either bulk distribution or packaging systems for final product disposition.

Other processes used to a much lesser extent include microsuspenion, emulsion, and solution polymerization. Microsuspension polymerization is basically similar to suspension polymerization, but homogenization of the monomer in water gives particle sizes in the 0.3-1 micron range. Emulsion polymerization takes place in a soap micelle where a small amount of monomer dissolves. When radicals from the water-soluble initiator enter the micelle, polymerization takes place. Additional monomer is supplied by diffusion through the water phase. Solution polymerization occurs in a solvent for the monomer and is often used to obtain very uniform copolymers of VCM with vinyl acetate and sometimes maleic acid. Mass or bulk polymerization is difficult due to the high viscosity accompanying high conversion, impeding agitation and heat removal. Although drying energy is saved, unreacted monomer is difficult to remove, even under vacuum. Mass PVC uses a PVC particle grown in liquid VCM without water.

The selection of process is dictated by the range of end products required. Only in the commodity business is the choice between suspension and mass PVC made on cost grounds since the resins have similar properties. Location also affects the choice of process since the relative cost of each process depends on the cost of power, steam, demineralized water, labor, etc.

Since PVC is insoluble in VCM, all the polymerization processes for producing PVC can be considered mass processes with different droplet sizes. Although the chemistry of the reaction may be the same, the PVC particle shape, molecular weight, molecular defects, and product morphology are all determined by the process.

PVC production technology is now quite mature, with only minor ongoing improvements being made to the established process routes. As such, competitive advantage centers on such issues as:

- Upstream integration into VCM production and possibly even chlorine production if power costs are favorable
- Larger capacity reactors to obtain economies of scale in capital investment
- More sophisticated control systems to reduce production costs and provide better and more consistent product quality
- Improved anti-scale agents to increase the number of batches between mechanical cleaning of the reactors
- Improved production additive packages for better base resin properties
- Improved compounding additive packages to improve performance and tailor compounds for new applications
Industry Status

The PVC business is presently in a state of considerable flux. Low prices and margins have resulted from considerable overcapacity exacerbated by reduced demand largely as a result of the global economic slow-down. The response to low profitability has been a round of industry cost-cutting and closure of old, high cost capacity.

In recent years the PVC industry has been asked to respond to challenges put forth by environmental activists:

- Use of chlorine in regard to the potential for atmospheric ozone depletion and global warming
- Control of carcinogenic VCM during its manufacture, polymerization to PVC, and fabrication of PVC products
- Residual monomer in PVC products
- Toxic and potential endocrine-disrupting effects of various additives used in PVC compounds
- Perceived difficulty in recycling PVC used in short lifetime applications
- Possible leaching of hazardous materials due to landfilling of PVC
- Possible formation of dioxins from incineration of PVC

Economics

The report develops cost of production estimates for suspension, mass, emulsion, and microsuspension PVC processes, taking into account higher scrap (off spec) rates for smaller facilities resulting from the need to make frequent grade changes. Cost plus ROCE values range from about $800 per ton to $1,150 per ton depending on process and size, on the basis of a US Gulf Coast location in third quarter 2003.

End Uses

The rigid pipe market represents almost one half of global PVC demand, so PVC has vigorously defended its competitive position against traditional construction materials such as cast iron, clay, and asbestos cement on the one hand and against other plastics such as high density polyethylene (HDPE), polypropylene, and acrylonitrile/butadiene/styrene (ABS) on the other. PVC accounts for about 83 percent of the total plastic pipe market; HDPE has about 14 percent and polypropylene and ABS share the remainder.

PVC has proved successful as a siding (i.e. cladding) material in preference to wood because of PVC’s low maintenance requirement. PVC is less energy intense and quieter in use (no noise from expansion and contraction) than aluminum. Vinyl siding will not dent, warp, crack, or
support rot or mildew. Resistance to termites, salt water, and air pollutants provides durability. Color that is an integral part of the material gives freedom from cracking, peeling, scratching, and wear. Vinyl’s inherent electrical resistance and flame retardance give added measures of safety over aluminum and wood, respectively.

Rigid profiles such as window frames are not subject to much interpolymer competition since PVC possesses a favorable price/performance balance. PVC offers maintenance advantages over soft woods and purchase cost advantages over hard woods and aluminum. Improved light stabilizer systems have extended PVC’s applicability to areas with high UV exposure.

Vinyl wire insulation provides the electrical and physical properties necessary to meet most building wiring requirements. There are several hundred UL-listed vinyl compounds designed especially for insulating and jacketing applications. Flexible vinyl is the major material used in wire and cable insulation and sheathing for telephone systems, electronic equipment, electrical apparatus and cords, power distribution lines, and automotive components, accounting for approximately 40 percent of the wire insulation and sheathing market. Vinyl offers many important properties in this application: dielectric behavior, elongation, and resistance to cutting/crushing, resistance to oil exposure, resistance to embrittlement, and resistance to UV light degradation.

Vinyl can also be used in rigid products such as electrical, electronic, and communications raceways; conduit systems for fiber optic cable; non-metallic work boxes, receptacles, and switch and outlet boxes; and utility ducts.

PET is inherently superior for sparkling water bottles and its higher clarity and perceived better recyclability have also helped it replace PVC in water bottle applications. However, PVC has maintained its market volume in cosmetics packaging and containers for edible oils.

Intermaterial competition in film and sheet is primarily PVC against other thermoplastics. PVC has only about 5 percent of the total U.S. and West European film and sheet markets. However, the versatility of PVC compounds allows a diverse range of rigid and flexible products to meet competition in the highly segmented film and sheet market. Flexible, transparent PVC cling film is used for commercial and household food wrapping, but has suffered stagnated growth due to concerns about plasticizer migration into fatty foods. Shelf life with PVC film is generally superior to that with polyethylene, as a result of PVC’s barrier properties to bacteria.

Rigid PVC sheet is thermoformed into packaging and finds some competition from polypropylene in larger segments and polyethylene terephthalate (PET) in specialized segments. Heavier gauge sheet is used as a low cost material for opaque cladding panels and glazing.

In flooring PVC competes with linoleum, carpet, wood, and ceramics. PVC has a good market share compared to these materials in the home kitchen/bathroom sector and in institutions where low cost
and wear ability are of paramount importance. Vinyl is favored in hospitals for its ability to be readily cleaned and sanitized.

PVC is strong, flexible, sterilizable, optionally transparent, and low in cost. Thus, its good price/performance balance is valued in applications from garden hoses to foodstuff handling to medical tubing. In the last two areas, polyolefins and fluoropolymers have made inroads on environmental grounds. However, PVC blood bags provide significantly longer blood storage life and advantageous dispensing characteristics relative to other materials.

PVC compounds have been developed targeting business machine housings. ABS holds a position of first choice in this area, albeit with some problems. While capable of attaining fire ratings of UL94 V1 and V0 with relative ease, achieving a 5-V requirement was difficult, and the brominated fire retardants required by ABS to impart flame retardancy were themselves subject to environmental scrutiny. PVC has the inherent ability to reach V0 without recourse to any additional fire retardants, but does not have as high a softening point as ABS. Compounds were developed based on resins offering low shear and easy flow in the molding machine in combination with a number of additive systems based around styrene maleic anhydride to improve the heat distortion behavior. However, costs of PVC formulations needed to mimic ABS’s performance were not sufficiently less than those of ABS to overcome PVC’s unpopularity with the molding companies due to corrosion problems.

Essentially all major PVC end-uses can be considered as mature, though some, such as rigid PVC applications in the construction market, are still exhibiting good growth. Conversely, most flexible PVC applications are exhibiting flat or even declining demand.

Growth areas for rigid PVC compounds include fencing and decking. Most other rigid PVC end-uses, such as siding, pipe, and door and window profiles are also gaining market share.

One area offering potential for rigid PVC is in wood-like profiles containing high amounts of wood filler. These profiles can be fabricated just like wood, but will not decay or rot. Applications include outdoor furniture, decking and the like. Other polymers, notably the polyolefins, are also targeting this market.

Much of the focus in flexible PVC end-uses is in the development of improved heat stabilizer and plasticizer formulations replacing lead-based and phthalate additive packages respectively. Candidates for heat stabilizer packages include calcium-zinc and other proprietary formulations. Candidates to replace phthalates include benzoates, citrates, glycolates, modified vegetable oils, and even polyolefin elastomers. A growth area for flexible PVC is gloves, replacing latex gloves on the basis of concerns over possible allergic reactions to latex.

Longer-term potential developments in PVC include the use of nanocomposite formulations designed to improve certain properties such as stiffness, fire resistance, and heat stability. Research is under way to investigate the use of novel polymerization techniques to remove structural defects
from the PVC chain, resulting in a far more thermally stable polymer. Such techniques also offer the potential to produce an internally plasticized PVC polymer by incorporating a medium-chain olefin, or by polymerizing other polar monomers.

The environmental aspects of PVC use are discussed at length in the report.

PVC supply and demand are detailed for the United States, Western Europe, and Asia Pacific, with a global overview as well.