

## A brief on polyvinyl chloride.

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### Editorial

Polyvinyl chloride is the world's third-most widely produced synthetic plastic polymer (after polyethylene and polypropylene). About 40 million tons of PVC are produced each year.

PVC comes in two basic forms: Rigid (sometimes abbreviated as RPVC) and flexible. The rigid form of PVC is used in construction for pipe and in profile applications such as doors and windows. It is also used in making bottles, non-food packaging, food-covering sheets, and cards (such as bank or membership cards). It can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is also used in plumbing, electrical cable insulation, imitation leather, flooring, signage, phonograph records, inflatable products, and many applications where it replaces rubber. With cotton or linen, it is used in the production of canvas.

Pure polyvinyl chloride is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran. PVC was synthesized in 1872 by German chemist Eugen Baumann after extended investigation and experimentation. The polymer appeared as a white solid inside a flask of vinyl chloride that had been left on a shelf sheltered from sunlight for four weeks. In the early 20th century, the Russian chemist Ivan Ostromislensky and Fritz Klatt of the German chemical company Griesheim-Elektron both attempted to use PVC in commercial products, but difficulties in processing the rigid, sometimes brittle polymer thwarted their efforts. Waldo Semon and the B.F. Goodrich Company developed a method in 1926 to plasticize PVC by blending it with various additives. The result was a more flexible and more easily processed material that soon achieved widespread commercial use.

Polyvinyl chloride is produced by polymerization of the Vinyl Chloride Monomer (VCM). About 80% of production involves suspension polymerization. Emulsion polymerization accounts for about 12%, and bulk polymerization accounts for 8%. Suspension polymerization affords particles with average diameters of 100-180  $\mu\text{m}$ , whereas emulsion polymerization gives much smaller particles of average size around 0.2  $\mu\text{m}$ . VCM and water are introduced into the reactor along with a polymerization initiator and other additives. The contents of the reaction vessel are pressurized and continually mixed to maintain the suspension and ensure a uniform particle size of the PVC resin. The reaction is exothermic and thus requires cooling. As the volume is reduced during the reaction (PVC is denser than VCM), water is continually added to the mixture to maintain the suspension.

The polymerization of VCM is started by compounds called initiators that are mixed into the droplets. These compounds break down to start the radical chain reaction. Typical initiators include dioctanoyl peroxide and dicetyl peroxydicarbonate, both of which have fragile oxygen-oxygen bonds. Some initiators start the reaction rapidly but decay quickly, and other initiators have the opposite effect. A combination of two different initiators is often used to give a uniform rate of polymerization. After the polymer has grown by about 10 times, the short polymer precipitates inside the droplet of VCM, and polymerization continues with the precipitated, solvent-swollen particles. The weight average molecular weights of commercial polymers range from 100,000 to 200,000, and the number average molecular weights range from 45,000 to 64,000.

Once the reaction has run its course, the resulting PVC slurry is degassed and stripped to remove excess VCM, which is recycled. The polymer is then passed through a centrifuge to remove water. The slurry is further dried in a hot air bed, and the resulting powder is sieved before storage or pelletization. Normally, the resulting PVC has a VCM content of less than 1 part per million. Other production processes, such as micro-suspension polymerization and emulsion polymerization, produce PVC with smaller particle sizes (10  $\mu\text{m}$  vs. 120-150  $\mu\text{m}$  for suspension PVC) with slightly different properties and with somewhat different sets of applications.

PVC may be manufactured from either naphtha or ethylene feedstock. However, in China, where there are substantial stocks, coal is the main starting material for the calcium carbide process. The acetylene so generated is then converted to VCM which usually involves the use of a mercury-based catalyst. The process is also very energy intensive with much waste generated.

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