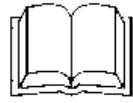


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# **Review of Polyvinyl Chloride Market in the CIS**

*Demo*

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## Introduction

### **Polyvinyl chloride (PVC): history, properties, uses**

Polyvinyl chloride (PVC, or simply vinyl) is a flexible or rigid material that is chemically nonreactive. PVC is composed of two simple building blocks: chlorine, based on common salt, and ethylene, from crude oil. The resulting compound, ethylene dichloride, is converted at very high temperatures to vinyl chloride monomer (VCM) gas. Through the chemical reaction known as polymerization, VCM becomes a chemically stable powder, polyvinyl chloride resin (PVC).

PVC was synthesized first in 1835 by a French chemist V. Regnault, but the discovery had no commercial results that time and had been practically forgotten. The second, commercial birth of PVC took place in the 20<sup>th</sup> century. A rubber scientist during the early 1920s stumbled onto a new material with fantastic properties during his search for a synthetic adhesive. Waldo Semon was intrigued with his finding, and experimented by making golf balls and shoe heels out of the versatile material called polyvinyl chloride, or PVC. The product was made commercially available in the United States (1933), Germany (1935), and Japan (1941), thanks to UCC succeeding in the development of the Bulk (Mass) Polymerization method.

Soon after “the second” discovery, PVC-based products such as insulated wire, raincoats and shower curtains hit the market. As more uses for vinyl were discovered, industry developed more ways to produce and process the new plastic.

Plants manufacturing PVC began to spring up during the '30s to meet demand for the versatile material. Just a decade after its conception, PVC - commonly known as vinyl - was sought for a variety of industrial applications including gaskets and tubing.

Vinyl manufacturers were working in high gear as World War II wound down, and they quickly found new markets for the durable plastic. Following the war, news of vinyl's versatility and flame-resistant properties spread, leading to dozens of commercial uses.

Five companies were making PVC at the century's midpoint, and innovative uses for vinyl continued to be found during the '50s and '60s. A vinyl-based latex was used on boots, fabric coatings and inflatable structures, and methods for enhancing vinyl's durability were refined, opening the door to applications in the building trades.

Vinyl products quickly became a staple of the construction industry; the plastic's resistance to corrosion, light and chemicals made it ideal for building applications. PVC piping was soon transporting water to thousands of homes and industries, aided by improvements in the material's resistance to extreme temperatures. Twenty companies were producing vinyl by 1980.

Today, vinyl is the second largest-selling plastic in the world, and the industry employs more than 100,000 people in the United States alone. Vinyl's low cost, versatility and performance make it the material of choice for dozens of industries such as health care, communications, aerospace, automotive, retailing, textiles and construction. Rigid as pipe or pliable as plastic wrap, vinyl is a leading material of the 21st century.

Vinyl is one of the most successful modern synthetic materials. It makes excellent use of resources and is suitable for a wide range of applications that surround us in everyday life. Products made of vinyl offer durability, fire resistance and energy efficiency, among other benefits. All these benefits have made vinyl the second-largest commodity plastic, for which demand continues to grow.

Because PVC resin can be combined with many additives and modifiers, vinyl can meet the requirements for products in many industries.

Vinyl is often chosen over other materials because of its low cost, versatility and performance properties.

Vinyl is strong, durable, abrasion and moisture resistant; withstands rust and corrosion; is electrically non-conductive and has excellent fire performance properties.

Vinyl can be produced in almost any color, with end products ranging from opaque to crystal-clear.

Through a variety of extrusion, calendaring and molding processes, vinyl is used in products as rigid as pipe or as flexible as upholstery and food wrap.

Because it is less than half petroleum, vinyl is the most energy-efficient plastic. And because it has been used for more than a half century, it is one of the world's most analyzed and tested materials.

Vinyl comes from salt, an inexpensive, renewable resource.

Vinyl products consume less energy, generate fewer emissions and save more energy than many competitive products.

Most vinyl products are durable and long-lived.

PVC has a broad range of applications, from high volume construction related products to simple electric wire insulation and coatings. Rigid PVC is easily machined, heat formed, welded, and even solvent cemented. PVC can also be machined using standard metal working tools and finished to close tolerances and finishes without great difficulty. PVC accepts paint and performs well under most silkscreening processes. PVC resins are normally mixed with other additives such as impact modifiers and stabilizers, providing hundreds of PVC based materials with a variety of engineering properties. There are three broad classifications for rigid PVC compounds: Type I, Type II, and CPVC. Type II varies from Type I due to greater impact values, but lower chemical resistance. CPVC has greater high temperature resistance. These materials are considered "unplasticized", because they are less flexible than the plasticized formulations. Type I, II and CPVC are normally available in rod, sheet, slab, pipe, tubular bar, fittings and valves. "Plasticized" PVC is available in sheet, film, fittings, flexible tubing, and pipe.

### Typical properties of polyvinyl chloride

ASTM test	Property	Rigid	Flexible
<b><i>PHYSICAL</i></b>			
D792	Specific gravity	1.30-1.58	1.20-1.70
D792	Specific volume (in. <sup>3</sup> /lb.)	20.5-19.1	-
D570	Water absorption, 24 hours, 1/8 inch thick (%)	0.04-0.4	0.15-0.75
<b><i>MECHANICAL</i></b>			
D638	Tensile strength (psi)	6,000-8,000	1,500-3,500
D638	Elongation (%)	50-150	200-450
D638	Tensile modulus (10~5 psi)	3.5-10	-
D790	Flexural modulus (10~5 psi)	3-8	-
D256	Impact strength, izod (ft-lb/in. of notch)	0.4-20.0	-
D785	Hardness, Shore	65-85D	50-100A
<b><i>THERMAL</i></b>			
C177	Thermal conductivity (10~4 cal-cm/sec-Sm~2-°C)	3.5-5.0	3.0-4.0
D696	Coefficient of thermal expansion (10~5 in./in.-°F)	1.2-5.6	3.9-13.9
D648	Deflection temperature (°F) At 264 psi At 66 psi	140-170 135-180	-
<b><i>ELECTRICAL</i></b>			
D149	Dielectric strength (V/mil) short time, 1/8-in. thick	350-500	300-400
D150	Dielectric constant At 1kHz	3.0-3.8	4.0-8.0
D150	Dissipation factor At 1kHz	0.009-0.017	0.07-0.16
D257	Volume resistivity (ohm-cm) At 73°F, 50% RH	>10~16	10~11 to 10~15
D495	Arc resistance(s)	60-80	-

## I. Technology of production of polyvinyl chloride and resources used

### I.1 Methods of production of polyvinyl chloride

How Is Vinyl Made? Like all plastic materials, vinyl results from a series of processing steps that convert hydrocarbon-based raw materials (petroleum, natural gas or coal) into unique synthetic products called polymers. The vinyl polymer is unusual, however, because it is based only in part on hydrocarbon feedstocks: ethylene obtained by processing, or cracking, natural gas or petroleum. The other half of the vinyl polymer is based on the natural element chlorine.

Chlorine gives vinyl two advantages. First, chlorine can be derived from brine - a solution of common salt and water, and a readily available, inexpensive commodity. Thus, vinyl is less sensitive to fluctuations in the world oil market than are totally oil dependent polymers. Second, chlorine has excellent inherent flame retardant properties. These properties are passed on directly to vinyl end-products, making vinyl an excellent choice for applications such as electrical conduit and wiring that require high resistance to ignition and flame spread.

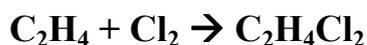
Through a chemical reaction, ethylene and chlorine combine to form ethylene dichloride, which, in turn, is transformed into a gas called vinyl chloride monomer (VCM). A final step, called "polymerization," converts the monomer into vinyl polymer, a fine-grained, white powder or resin known as polyvinyl chloride (PVC), or simply "vinyl." Vinyl resin, however, is still one step away from being a usable material: it must be combined with selected chemical additives and modifiers to achieve the various properties desired in vinyl end-products. Once these are added, the resulting material - vinyl compound - can be converted into an almost limitless range of applications. This versatility is yet another reason why vinyl claims such a large share of the plastics market. It is the only plastic that can be made thin and flexible enough for wall-coverings, yet rigid and tough enough for siding on buildings. Depending on the additives and modifiers used, vinyl compound can be used indoors or outside, be crystal clear or opaque, and matched to virtually any color in the rainbow.

#### Process Technology Overview

EDC/VCM VCM (vinyl chloride monomer) is made by cracking EDC (ethylene dichloride, 1,2-dichloroethane) to yield equimolar amounts of VCM and HCl (hydrogen chloride).



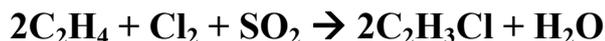
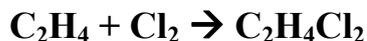
EDC is made by a direct chlorination process, in which chlorine is added to ethylene.



Half of the chlorine consumed by this reaction ends up as HCl when the EDC is cracked to VCM. This HCl is recovered in the subsequent VCM purification step, and reacted with oxygen and additional ethylene in the oxychlorination process to make more EDC.



Combining these three reaction steps into an integrated operation forms the basis for the balanced VCM process, in which vinyl chloride is made from chlorine, ethylene, and oxygen.

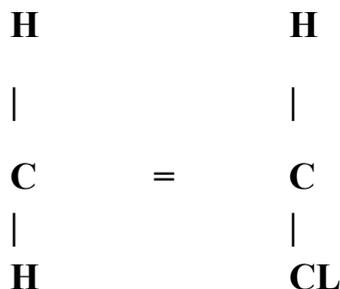


Other components of the VCM process include VCM Purification, EDC Purification, Hydrogenation, and By-product Separation and Disposal.

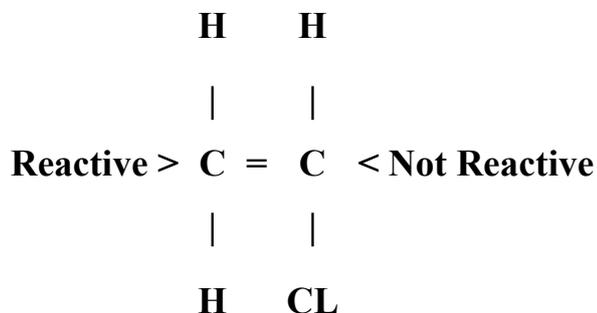
Besides, in smaller volumes (for instance, in CIS), so-called “acetylene process”, based on use of acetylene and hydrochloric acid, is applied in VCM production.

### Reaction chemistry

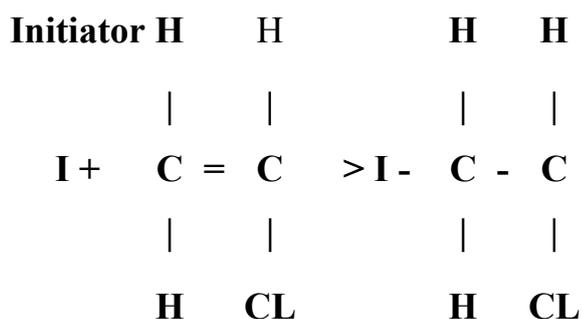
VCM is a gas at ambient temperature and pressure and can be represented chemically as follows:



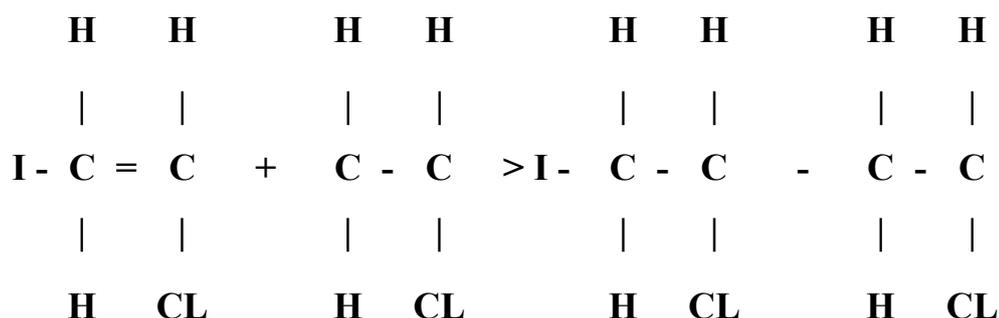
Notice the carbon to carbon double bond. Converting the vinyl chloride monomer to the polymer PVC involves a reaction that breaks this double bond. The reaction is centered at the double bond and the other atoms are unaffected:



When an initiator is added to the reaction medium, the VCM becomes more reactive, breaking the double bond. This happens because the attraction between the carbons in the VCM molecule is less than the attraction between the carbons and the initiator. The initiator is carefully selected to insure that this is the case. With the initiator, double bonds are broken and single bonds are re-established on the VCM:



The newly created single bond is now lacking the fourth bond for each carbon atom. This fourth bond requirement is fulfilled when it meets another VCM molecule in the following reaction:



Each time a vinyl chloride monomer is added, it creates another single bond where more VCM can be added. This chain reaction polymerization will continue as long as the growing chain can find monomer units to add to itself.

This reaction is exothermic, liberating approximately 1600 kJ/kg VCM. The heat created from the reaction comes from the breaking of the double bond in the vinyl chloride monomer. This heat must be removed in order to maintain temperature control, which in turn, is the key controller of molecular weight. This heat can be removed from the reactor by cooling water, refrigerated water, and ammonia refrigerant or by evaporative cooling.

The normal range of polymerization temperatures is 52-70°C. This temperature range produces resins with a molecular weight range of 40,000 to 73,000. The molecular weight is measured by determining the viscosity of a dilute polymer solution. The results are expressed in ISO viscosity numbers from which can be derived K-value. The K-value range of the vinyl resins is 57 to 74 with the higher numbers corresponding to higher molecular weights and lower reaction temperatures.

The molecular weight can be altered by the use of additives to the polymerization that act as chain transfer agents. Chain transfer agents are used to reduce the molecular weight normally produced by a specific reaction temperature by terminating the chains earlier than would normally occur. They are useful if the reaction temperature necessary to give a desired molecular weight is too high for the equipment because of excessive pressures.

During reaction, the reaction temperature and the resulting partial pressures determine the pressure in the reactor. As the trapped VCM is not readily available, it does not contribute to the reactor pressure. Thus, as the reaction continues more and more VCM is being swollen into the PVC/VCM gel. When the conversion reaches 75%, almost all of the free VCM has been reacted. Further reaction occurs nearly

exclusively in the gel phase. At this point the reaction is starved for free VCM and this causes a drop in the partial pressure exerted by the free VCM. This drop is very dramatic and is seen quite clearly on the reactor's pressure transmitters. The drop in pressure is directly proportional to VCM/PVC conversion. A pressure drop of 1 kg/cm<sup>2</sup> over the normal reaction pressure, for instance, corresponds to an 82% conversion.

### Commercial PVC Process Technologies

There are **three basic polymerization processes** used to produce PVC commercially - **bulk, emulsion** and **suspension**. All the processes are based on free-radical polymerization of vinyl chloride monomer, using initiators such as organic peroxides. The choice of polymerization method depends on the ultimate application of the resin and the economics of the processes.

1) Of the processes, the **suspension** method is the most widely used. The following is an overview of the suspension PVC manufacturing process technology as licensed by OxyVinyls company, the third greatest supplier of PVC resin in the world and the largest in North America.

Coating the reactor internal surfaces with an anti-stick material starts the suspension PVC production cycle. This is the key part of the clean reactor technology that enables the OxyVinyls process to produce over 300 charges without opening the reactor for cleaning. After the coating cycle, the VCM, water, emulsifiers and initiator are added to the pressure rated reactor. The quantities of these ingredients are measured to a very high degree of accuracy. This minimizes batch to batch variability from the reactors.

As a result of the polymerization, heat is generated during this exothermic reaction. This heat must be removed to maintain the correct reaction temperature. We have experience removing this heat utilizing several media including cooling tower water, refrigerated water and ammonia in concert with several specialized heat removal systems. With distributed computer control systems and state of the art temperature control schemes, we are able to maintain the reaction temperature very close to setpoint.

The reaction is stopped when the proper conversion from VCM to PVC is achieved. Once again, sophisticated measurements permit a consistently accurate endpoint determination. Once the reaction is terminated, the unreacted VCM is partially recovered in the reactor. When the polymerizer is at nearly atmospheric pressure, the PVC slurry and unreacted VCM are pumped to the column feed tank. At this point the process switches from batch operation to continuous operation. The column feed tank serves as a surge tank between the batch reactors and the continuous slurry stripping column.

In the column feed tank, unreacted VCM is partially recovered for recycle. The remaining VCM is removed in the slurry stripping column and sent to recovery. This recovered VCM is condensed, stored and used in subsequent reactions.

From the stripping column the slurry passes through a continuous centrifuge to remove the majority of the water. The wetcake drops from the centrifuge and enters

the dryer. Fluid bed or rotary dryers are viable depending upon local preference and marketing situations.

At the discharge of the dryer, the PVC drops first through a magnet to remove metal particles, then through a screener to remove any oversized resin. Finally, the prime resin is pneumatically transferred to the resin silos.

The suspension process currently dominates in PVC commercial production worldwide and in the CIS too, it yields around 80% of world PVC.

2) **Emulsion** Polymerization is basically very similar to the suspension process, except that relatively large amounts of emulsifying agents are used. In this process, the monomers are emulsified or dispersed as fine droplets in a large amount of nonsolvent, usually water. When the reaction is complete, the polymerized product is still dispersed as an emulsion or latex. This process produces resins with a very small particle size and typically of higher molecular weight than the suspension resins. To maintain the small particle size, emulsion resins are usually dried using a spray drying technique. The disadvantage of this method is that impurities left in the product may damage electrical and other properties - complete removal of the emulsifiers is never achieved in resins produced by this process so that products requiring high clarity, for example, packaging film or very low water adsorption, such as wire insulation, cannot be produced from emulsion resins. The resulting powders are called paste resins or dispersion resins.

Around 10% of world PVC are made by the emulsion method. In the CIS this method is of minor importance compared with the suspension polymerization.

3) **Bulk (Mass)** Polymerization: The monomers are polymerized in the absence of solvent or diluent. Since the reaction is strongly exothermic, the process is conducted in small vessels and the ambient temperature is lowered as the reaction proceeds. The reactors are specially designed to handle bulk polyvinyl chloride at elevated temperatures.

These bulk polymers have several desirable features - high porosity (desirable in making flexible compound), clarity, and relatively uniform shape and size of the particles. They also have remarkably good heat stability and improved fusion properties, and can be processed with the ease of conventional vinyl chloride-vinyl acetate copolymers. Bulk-polymerized resins resemble the suspension resins and are used in the same applications.

Around 10% of world PVC are made by the bulk method; in the CIS, the method is not applied at all.

The bulk of design capacities on PVC production, available in the CIS, refers to output of suspension PVC (see Table 1).