Polyvinyl chloride

Polyvinyl chloride (/_pplivaInəl 'klɔːraId/;^[5] colloquial: **polyvinyl**, **vinyl**;^[6] abbreviated: **PVC**) is the world's third-most widely produced synthetic <u>plastic polymer</u>, after <u>polyethylene</u> and <u>polypropylene</u>.^[7] About 40 million tonnes are produced per 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,^[8] 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,^[9] inflatable products, and many applications where it replaces rubber.^[10] With cotton or linen, it is used to make <u>canvas</u>.

Pure polyvinyl chloride is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran.

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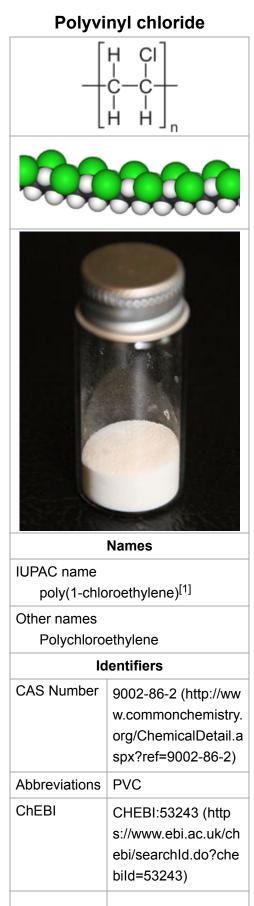
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Discovery

PVC was accidentally synthesized in 1872 by German chemist Eugen Baumann.^[11] The polymer appeared as a white solid inside a flask of vinyl chloride that had been left exposed to sunlight. In the early 20th century the Russian chemist <u>Ivan Ostromislensky</u> and <u>Fritz Klatte</u> 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. <u>Waldo Semon and the B.F. Goodrich Company</u> developed a method in 1926 to <u>plasticize</u> PVC by blending it with various additives. The result was a more flexible and more easily processed material that soon achieved widespread commercial use.

Production

Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer (VCM), as shown.^[12]

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MeSH	Polyvinyl+Chloride (https://www.nlm.nih. gov/cgi/mesh/2014/ MB_cgi?mode=&ter m=Polyvinyl+Chlorid e)			
CompTox Dashboard (EPA)	DTXSID5025940 (htt ps://comptox.epa.go v/dashboard/DTXSI D5025940) 🖍			
Properties				
Chemical formula	(C ₂ H ₃ CI) _n ^[2]			
Magnetic susceptibility (\chi)	−10.71×10 ^{−6} (SI, 22 °C) ^[3]			
are given for m	otherwise noted, data naterials in their (at 25 °C [77 °F],			

none

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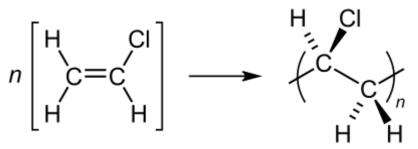
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Infobox references

Mechanical properties

Elongation at break	20–40%		
Notch test	2–5 kJ/m ²		
Glass Transition Temperature	82 °C (180 °F) ^[4]		
Melting point	100 °C (212 °F) to 260 °C (500 °F) ^[4]		
Effective heat of combustion	17.95 MJ/kg		
Specific heat	0.9 kJ/(kg·K)		

Polyvinyl chloride - Wikipedia



(<i>c</i>)	
Water	0.04–0.4
absorption	
(ASTM)	
Dielectric	40 MV/m
Breakdown	
Voltage	

About 80% of production involves suspension polymerization. Emulsion polymerization accounts for about 12%, and bulk

<u>polymerization</u> accounts for 8%. Suspension polymerization affords particles with average diameters of 100–180 μ m, whereas emulsion polymerization gives much smaller particles of average size around 0.2 μ 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 <u>exothermic</u> 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.^[7]

The polymerization of VCM is started by compounds called initiators that are mixed into the droplets. These compounds break down to start the <u>radical chain reaction</u>. Typical initiators include dioctanoyl <u>peroxide</u> and dicetyl peroxydicarbonate, both of which have fragile O-O 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 <u>weight average molecular weights</u> 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 μ m vs. 120–150 μ m for suspension PVC) with slightly different properties and with somewhat different sets of applications.

PVC may be manufactured from either <u>naphtha</u> or <u>ethylene</u> feedstock.^[13] However, in China, where there are substantial stocks, coal is the main starting material for the <u>Calcium carbide</u> process. The <u>acetylene</u> so generated is then converted to VCM which usually involves the use of a <u>mercury</u> based catalyst. The process is also very energy intensive with much waste generated.

Microstructure

The polymers are linear and are strong. The monomers are mainly arranged head-to-tail, meaning that there are chlorides on alternating carbon centres (https://i.stack.imgur.com/mGdHr.png). PVC has mainly an atactic stereochemistry, which means that the relative stereochemistry of the chloride centres (https://chlorine.americanchemistry.com/uploadedImages/chlorine/Site_Content/_Image_Library/Content_Image/PVC-Production-3.jpg) are random. Some degree of syndiotacticity of the

chain gives a few percent crystallinity that is influential on the properties of the material. About 57% of the mass of PVC is <u>chlorine</u>. The presence of chloride groups gives the polymer very different properties from the structurally related material <u>polyethylene</u>.^[14] The density is also higher than these structurally related plastics.

Producers

About half of the world's PVC production capacity is in <u>China</u> despite the closure of many Chinese PVC plants due to issues complying with environmental regulations and poor capacities of scale. The largest single producer of PVC as of 2018 is <u>Shin-Etsu Chemical</u> of Japan, with a global share of around 30%.^[13] The other major suppliers are based in North America and Western Europe.

Additives

The product of the polymerization process is unmodified PVC. Before PVC can be made into finished products, it always requires conversion into a compound by the incorporation of additives (but not necessarily all of the following) such as heat stabilizers, <u>UV</u> stabilizers, plasticizers, processing aids, impact modifiers, thermal modifiers, fillers, flame retardants, <u>biocides</u>, blowing agents and smoke suppressors, and, optionally, pigments.^[15] The choice of additives used for the PVC finished product is controlled by the cost performance requirements of the end use specification (underground pipe, window frames, intravenous tubing and flooring all have very different ingredients to suit their performance requirements). Previously, polychlorinated biphenyls (PCBs) were added to certain PVC products as flame retardants and stabilizers.^[16]

Phthalate plasticizers

Most vinyl products contain <u>plasticizers</u> which dramatically improve their performance characteristic. The most common plasticizers are derivatives of phthalic acid. The materials are selected on their compatibility with the polymer, low volatility levels, and cost. These materials are usually oily colourless substances that mix well with the PVC particles. About 90% of the plasticizer market, estimated to be millions of tons per year worldwide, is dedicated to PVC.^[15]

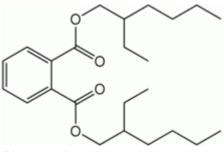
Di-2ethylhexylphthalate

While Di-2ethylhexylphthalate (DEHP) has been medically approved for many years for use in medical devices, it was permanently banned for use in children's products in the US in 2008 by US Congress;^[17] the PVC-DEHP combination had proved to be very suitable for making blood bags because DEHP stabilizes red blood cells, minimizing hemolysis (red blood cell rupture). However, DEHP is coming under increasing pressure in Europe. The assessment of potential risks related to phthalates, and in particular the use of DEHP in PVC medical devices, was subject to scientific and policy review by the European Union authorities, and on 21 March 2010, a specific labeling requirement was introduced across the EU for all devices containing phthalates that are classified as CMR (carcinogenic, mutagenic or toxic to reproduction).^[18] The label aims to enable healthcare professionals to use this equipment safely, and, where needed, take appropriate precautionary measures for patients at risk of over-exposure.

DEHP alternatives, which are gradually replacing it, are Adipates, Butyryltrihexylcitrate (BTHC), Cyclohexane-1,2-dicarboxylic acid, diisononylester (DINCH), Di(2-ethylhexyl)terephthalate, polymerics and trimellitic acid, 2-ethylhexylester (TOTM).

Metal stabilizers

Liquid mixed metal stabilisers are used in several PVC flexible applications such as <u>calendered</u> films, extruded profiles, injection moulded soles and footwear, extruded hoses and plastisols where PVC paste is spread on to a backing (flooring, wall covering, artificial leather). Liquid mixed metal stabiliser systems are primarily based on barium, zinc and calcium carboxylates. In general liquid mixed metals like BaZn, CaZn require the addition of co-stabilisers, antioxidants and organo-phosphites to provide optimum performance.



Bis(2-ethylhexyl) phthalate was a common plasticizer for PVC but is being replaced by higher molecular weight phthalates.

BaZn stabilisers have successfully replaced cadmium-based stabilisers in Europe in many PVC semi-rigid and flexible applications.^[19]

In Europe, particularly Belgium, there has been a commitment to eliminate the use of cadmium (previously used as a part component of heat stabilizers in window profiles) and phase out lead-based heat stabilizers (as used in pipe and profile areas) such as liquid autodiachromate and calcium polyhydrocummate by 2015. According to the final report of Vinyl $2010^{[20]}$ cadmium was eliminated across Europe by 2007. The progressive substitution of lead-based stabilizers is also confirmed in the same document showing a reduction of 75% since 2000 and ongoing. This is confirmed by the corresponding growth in **calcium-based** stabilizers, used as an alternative to lead-based stabilizers, more and more, also outside Europe.

Tin-based stabilizers are mainly used in Europe for rigid, transparent applications due to the high temperature processing conditions used. The situation in North America is different where tin systems are used for almost all rigid PVC applications. Tin stabilizers can be divided into two main groups, the first group containing those with tin-oxygen bonds and the second group with tin-sulfur bonds.

Heat stabilizers

One of the most crucial additives are heat stabilizers. These agents minimize loss of HCl, a degradation process that starts above 70 °C (158 °F). Once dehydrochlorination starts, it is <u>autocatalytic</u>. Many diverse agents have been used including, traditionally, derivatives of <u>heavy metals</u> (lead, cadmium). Metallic soaps (metal "salts" of <u>fatty acids</u>) are common in flexible PVC applications, species such as <u>calcium stearate</u>.^[7] Addition levels vary typically from 2% to 4%. Tin Mercaptides are widely used globally in rigid PVC applications due to their high efficiency and proven performance. Typical usage levels are 0.3 (pipe) to 2.5phr (foam) depending on the application. Tin stabilizers are the preferred stabilizers for high output PVC and CPVC extrusion. Tin stabilizers have been in use for over 50 years by companies such as PMC Organometallix and its predecessors. The choice of the best PVC stabilizer depends on its cost effectiveness in the end use application, performance specification requirements, processing technology and regulatory approvals.

Properties

PVC is a <u>thermoplastic</u> polymer. Its properties are usually categorized based on rigid and flexible PVCs.

Property	Unit of measurement	Rigid PVC	Flexible PVC
Density ^[21]	g/cm ³	1.3–1.45	1.1–1.35
Thermal conductivity ^[22]	W/(m·K)	0.14–0.28	0.14–0.17
Yield strength ^[21]	psi	4,500–8,700	31–60
	<u>MPa</u>	1,450–3,600	10.0–24.8
Young's modulus ^[23]	psi	490,000	—
	<u>GPa</u>	3.4	—
Flexural strength (yield) ^[23]	psi	10,500	—
	МРа	72	—
Compression strength ^[23]	psi	9,500	—
	МРа	66	_
Coefficient of thermal expansion (linear) ^[23]	mm/(mm °C)	5×10 ⁻⁵	
Vicat B ^[22]	°C	65–100	Not recommended
Resistivity ^{[24][25]}	<u>Ω</u> m	10 ¹⁶	10 ¹² –10 ¹⁵
Surface resistivity ^{[24][25]}	Ω	10 ¹³ –10 ¹⁴	10 ¹¹ –10 ¹²

Mechanical

PVC has high hardness and mechanical properties. The mechanical properties enhance with the molecular weight increasing but decrease with the temperature increasing. The mechanical properties of rigid PVC (uPVC) are very good; the <u>elastic modulus</u> can reach 1500-3,000 MPa. The soft PVC (flexible PVC) elastic limit is 1.5–15 MPa.

Thermal and fire

The <u>heat stability</u> of raw PVC is very poor, so the addition of a heat <u>stabilizer</u> during the process is necessary in order to ensure the product's properties. Traditional product PVC has a maximum operating temperature around 140 °F (60 °C) when heat distortion begins to occur.^[26] Melting temperatures range from 212 °F (100 °C) to 500 °F (100 °C to 260 °C) depending upon manufacture additives to the PVC. The linear expansion coefficient of rigid PVC is small and has good flame retardancy, the <u>limiting oxygen index</u> (LOI) being up to 45 or more. The LOI is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer and noting that air has 20% content of oxygen.

As a thermoplastic, PVC has an inherent insulation that aids in reducing condensation formation and resisting internal temperature changes for hot and cold liquids.^[26]

Electrical

PVC is a polymer with good insulation properties, but because of its higher polar nature the electrical insulating property is inferior to non-polar polymers such as polyethylene and polypropylene.

Since the dielectric constant, dielectric loss tangent value, and volume resistivity are high, the corona resistance is not very good, and it is generally suitable for medium or low voltage and low frequency insulation materials.

Chemical

PVC is chemically resistant to acids, salts, bases, fats, and alcohols, making it resistant to the corrosive effects of sewage, which is why it is so extensively utilized in sewer piping systems. It is also resistant to some solvents, this, however, is reserved mainly for uPVC (unplasticized PVC). Plasticized PVC, also known as PVC-P, is in some cases less resistant to solvents. For example, PVC is resistant to fuel and some paint thinners. Some solvents may only swell it or deform it but not dissolve it, but some, like tetrahydrofuran or acetone, may damage it.

Applications

Pipes

Roughly half of the world's polyvinyl chloride resin manufactured annually is used for producing pipes for municipal and industrial applications.^[27] In the water distribution market, it accounts for 66% of the market in the U.S., and in sanitary sewer pipe applications, it accounts for 75%.^{[28][29]} Buried PVC pipes in both water and sanitary sewer applications that are 4 inches (100 mm) in diameter and larger are typically joined by means of a gasketsealed joint. The most common type of gasket utilized in North America is a metal reinforced elastomer, commonly referred to as a Rieber sealing system.^[30] Its light weight, low cost, and low maintenance make it attractive. However, it must be carefully installed and bedded to ensure longitudinal cracking and overbelling does not occur. Additionally, PVC pipes can be fused together using various solvent cements, or heat-fused (buttfusion process, similar to joining high-density polyethylene (HDPE) pipe), creating permanent joints that are virtually impervious to leakage.



PVC is used extensively in sewage pipes due to its low cost, chemical resistance and ease of jointing

In February 2007 the California Building Standards Code was updated to approve the use of chlorinated polyvinyl chloride (CPVC) pipe for use in residential water supply piping systems. CPVC has been a nationally accepted material in the U.S. since 1982; California, however, has permitted only limited use since 2001. The Department of Housing and Community Development prepared and certified an <u>environmental impact statement</u> resulting in a recommendation that the commission adopt and approve the use of CPVC. The commission's vote was unanimous, and CPVC has been placed in the 2007 California Plumbing Code.

Electric cables

PVC is commonly used as the <u>insulation</u> on <u>electrical cables</u> such as <u>teck</u>; PVC used for this purpose needs to be plasticized. Flexible PVC coated wire and cable for electrical use has traditionally been stabilised with lead, but these are being replaced with calcium-zinc based systems.

In a fire, PVC-coated wires can form <u>hydrogen chloride</u> fumes; the chlorine serves to scavenge <u>free</u> <u>radicals</u> and is the source of the material's <u>fire retardance</u>. While hydrogen chloride fumes can also pose a <u>health hazard</u> in their own right, it dissolves in moisture and breaks down onto surfaces, particularly in areas where the air is cool enough to breathe, and is not available for inhalation.^[31] Frequently in applications where smoke is a major hazard (notably in tunnels and communal areas), PVC-free cable insulation is preferred, such as low smoke zero halogen (LSZH) insulation.

Construction

PVC is a common, strong but lightweight plastic used in construction. It is made softer and more flexible by the addition of plasticizers. If no plasticizers are added, it is known as uPVC (unplasticized polyvinyl chloride) or rigid PVC.

uPVC is extensively used in the building industry as a lowmaintenance material, particularly in Ireland, the United Kingdom, in the United States and Canada. In the U.S. and Canada it is known as vinyl or vinyl siding.^[32] The material comes in a range of colors and finishes, including a photo-effect wood finish, and is used as a substitute for painted wood, mostly for window frames and sills when installing insulated glazing in new buildings; or to replace older single-glazed windows, as it does not decompose and is weather-resistant. Other uses include



"A modern Tudorbethan" house with uPVC gutters and downspouts, fascia, decorative imitation "halftimbering", windows, and doors

fascia, and siding or weatherboarding. This material has almost entirely replaced the use of cast iron for plumbing and drainage, being used for waste pipes, drainpipes, gutters and downspouts. uPVC is known as having strong resistance against chemicals, sunlight, and oxidation from water.^[33]

Signs

Polyvinyl chloride is formed in flat sheets in a variety of thicknesses and colors. As flat sheets, PVC is often expanded to create voids in the interior of the material, providing additional thickness without additional weight and minimal extra cost (see <u>Closed-cell PVC foamboard</u>). Sheets are cut using saws and rotary cutting equipment. Plasticized PVC is also used to produce thin, colored, or clear, <u>adhesive</u>-backed films referred to simply as vinyl. These films are typically cut on a <u>computer</u>-controlled plotter (see Vinyl cutter) or printed in a wide-format printer.



Double glazed units

These sheets and films are used to produce a wide variety of <u>commercial signage</u> products, including car body stripes and stickers.

Clothing

<u>PVC fabric</u> is <u>water-resistant</u>, used for its weather-resistant qualities in coats, skiing equipment, shoes, <u>jackets</u>, <u>aprons</u>, and sports bags.

PVC fabric has a niche role in speciality clothing, either to create an <u>artificial leather</u> material or at times simply for its effect. <u>PVC</u> <u>clothing is common in Goth, Punk, clothing fetish</u> and <u>alternative</u> <u>fashions</u>. PVC is less expensive than <u>rubber</u>, <u>leather</u> or <u>latex</u>, which it is used to simulate.

Healthcare

The two main application areas for <u>single-use</u> medically approved PVC compounds are flexible containers and tubing: containers used for blood and blood components, for urine collection or for ostomy products and tubing used for blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets etc. In Europe the consumption of PVC for medical devices is



Black PVC trousers

approximately 85,000 tons each year. Almost one third of plastic-based medical devices are made from PVC.^[34] The reasons for using flexible PVC in these applications for over 50 years are numerous and based on cost effectiveness linked to transparency, light weight, softness, tear strength, kink resistance, suitability for sterilization and biocompatibility.

Flooring

Flexible PVC <u>flooring</u> is inexpensive and used in a variety of buildings, including homes, hospitals, offices, and schools. Complex and <u>3D</u> designs are possible, which are then protected by a clear wear layer. A middle vinyl foam layer also gives a comfortable and safe feel. The smooth, tough surface of the upper wear layer prevents the buildup of dirt, which prevents microbes from breeding in areas that need to be kept sterile, such as hospitals and clinics.

Wire rope

PVC may be <u>extruded</u> under pressure to encase <u>wire rope</u> and aircraft cable used for general purpose applications. PVC coated wire rope is easier to handle, resists corrosion and abrasion, and may be color-coded for increased visibility. It is found in a variety of industries and environments both indoor and out.^[35]

PVC has been used for a host of consumer products. One of its earliest mass-market consumer applications was <u>vinyl record</u> production. More recent examples include wallcovering, greenhouses, home playgrounds, foam and other toys, custom truck toppers (<u>tarpaulins</u>), ceiling tiles and other kinds of interior cladding.

PVC piping is cheaper than metals used in musical instrument making; it is therefore a common alternative when making instruments, often for leisure or for rarer instruments such as the <u>contrabass</u> flute.^[36]

Chlorinated PVC

PVC can be usefully modified by chlorination, which increases its chlorine content to or above 67%. Chlorinated polyvinyl chloride, (CPVC), as it is called, is produced by chlorination of aqueous solution of suspension PVC particles followed by exposure to UV light which initiates the free-radical chlorination.^[7] The reaction produces CPVC, which has thermal and chemical properties that are superior to PVC.

Health and safety

Degradation

Degradation during service life, or after careless disposal, is a chemical change that drastically reduces the average molecular weight of the polyvinyl chloride polymer. Since the mechanical integrity of a plastic depends on its high average molecular weight, wear and tear inevitably weakens the material. Weathering degradation of plastics results in their surface embrittlement and microcracking, yielding microparticles that continue on in the environment. Also known as <u>microplastics</u>, these particles act like sponges and soak up <u>persistent organic pollutants</u> (POPs) around them. Thus laden with high levels of POPs, the microparticles are often ingested by organisms in the biosphere.

However, there is evidence that three of the polymers (HDPE, LDPE, and PP) consistently soaked up POPs at concentrations an order of magnitude higher than did the remaining two (PVC and PET). After 12 months of exposure, for example, there was a 34-fold difference in average total POPs amassed on LDPE compared to PET at one location. At another site, average total POPs adhered to HDPE was nearly 30 times that of PVC. The researchers think that differences in the size and shape of the polymer molecules can explain why some accumulate more pollutants than others.^[37] The fungus Aspergillus fumigatus effectively degrades plasticized PVC.^[38] Phanerochaete chrysosporium was grown on PVC in a mineral salt agar.^[39] Phanerochaete chrysosporium, Lentinus tigrinus, Aspergillus niger, and Aspergillus sydowii can effectively degrade PVC.^[40]

Plasticizers

Phthalates, which are incorporated into plastics as plasticizers, comprise approximately 70% of the U.S. plasticizer market; phthalates are by design not covalently bound to the polymer matrix, which makes them highly susceptible to leaching. Phthalates are contained in plastics at high percentages. For example, they can contribute up to 40% by weight to intravenous medical bags and up to 80% by weight in medical tubing.^[41] Vinyl products are pervasive—including toys,^[42] car interiors, shower curtains, and flooring—and initially release chemical gases into the air. Some studies indicate that this outgassing of additives may contribute to health complications, and have resulted in a call for banning the use of DEHP on shower curtains, among other uses.^[43] Japanese car companies <u>Toyota</u>, <u>Nissan</u>, and <u>Honda</u> eliminated the use of PVC in car interiors since 2007.

In 2004 a joint Swedish-Danish research team found a statistical association between allergies in children and indoor air levels of DEHP and BBzP (<u>butyl benzyl phthalate</u>), which is used in vinyl flooring.^[44] In December 2006, the European Chemicals Bureau of the European Commission

released a final draft risk assessment of BBzP which found "no concern" for consumer exposure including exposure to children.^[45]

EU decisions on phthalates

Risk assessments have led to the classification of low molecular weight and labeling as Category 1B Reproductive agents. Three of these phthalates, DBP, BBP and DEHP were included on annex XIV of the <u>REACH</u> regulation in February 2011 and will be phased out by the EU by February 2015 unless an application for authorisation is made before July 2013 and an authorisation granted. DIBP is still on the REACH Candidate List for Authorisation. Environmental Science & Technology, a peer reviewed journal published by the American Chemical Society states that it is completely safe.^[46]

In 2008 the European Union's Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) reviewed the safety of DEHP in medical devices. The SCENIHR report states that certain medical procedures used in high risk patients result in a significant exposure to DEHP and concludes there is still a reason for having some concerns about the exposure of prematurely born male babies to medical devices containing DEHP.^[47] The Committee said there are some alternative plasticizers available for which there is sufficient toxicological data to indicate a lower hazard compared to DEHP but added that the functionality of these plasticizers should be assessed before they can be used as an alternative for DEHP in PVC medical devices. Risk assessment results have shown positive results regarding the safe use of High Molecular Weight Phthalates. They have all been registered for <u>REACH</u> and do not require any classification for health and environmental effects, nor are they on the Candidate List for Authorisation. High phthalates are not CMR (carcinogenic, mutagenic or toxic for reproduction), neither are they considered endocrine disruptors.

In the EU Risk Assessment the European Commission has confirmed that Di-isononyl phthalate (DINP) and Di-isodecyl phthalate (DIDP) pose no risk to either human health or the environment from any current use. The European Commission's findings (published in the EU Official Journal on 13 April 2006)^[48] confirm the outcome of a risk assessment involving more than 10 years of extensive scientific evaluation by EU regulators. Following the recent adoption of EU legislation with the regard to the marketing and use of DINP in toys and childcare articles, the risk assessment conclusions clearly state that there is no need for any further measures to regulate the use of DINP. In Europe and in some other parts of the world, the use of DINP in toys and childcare items has been restricted as a precautionary measure. In Europe, for example, DINP can no longer be used in toys and childcare items that can be put in the mouth even though the EU scientific risk assessment concluded that its use in toys does not pose a risk to human health or the environment. The rigorous EU risk assessments, which include a high degree of conservatism and built-in safety factors, have been carried out under the strict supervision of the European Commission and provide a clear scientific evaluation on which to judge whether or not a particular substance can be safely used.

The FDA Paper titled "Safety Assessment of Di(2-ethylhexyl)phthalate (DEHP)Released from PVC Medical Devices" states that [3.2.1.3] Critically ill or injured patients may be at increased risk of developing adverse health effects from DEHP, not only by virtue of increased exposure relative to the general population, but also because of the physiological and pharmacodynamic changes that occur in these patients compared to healthy individuals.^[49]

Lead had previously been frequently added to PVC to improve workability and stability. Lead has been shown to leach into drinking water from PVC pipes.^[50]

In Europe (EU 28) the use of lead-based stabilizers was gradually replaced. The <u>VinylPlus</u> voluntary commitment which began in 2000, saw European Stabiliser Producers Association (ESPA) members complete the replacement of Pb-based stabilisers in 2015.^{[51][52]}

Vinyl chloride monomer

In the early 1970s, the carcinogenicity of vinyl chloride (usually called vinyl chloride monomer or VCM) was linked to cancers in workers in the polyvinyl chloride industry. Specifically workers in polymerization section of a <u>B.F. Goodrich</u> plant near <u>Louisville</u>, Kentucky, were diagnosed with liver <u>angiosarcoma</u> also known as <u>hemangiosarcoma</u>, a rare disease.^[53] Since that time, studies of PVC workers in Australia, Italy, Germany, and the UK have all associated certain types of occupational cancers with exposure to vinyl chloride, and it has become accepted that VCM is a carcinogen.^[7] Technology for removal of VCM from products has become stringent, commensurate with the associated regulations.

Dioxins

PVC produces <u>HCl</u> upon combustion almost quantitatively related to its chlorine content. Extensive studies in Europe indicate that the chlorine found in emitted dioxins is not derived from HCl in the <u>flue gases</u>. Instead, most dioxins arise in the condensed solid phase by the reaction of inorganic chlorides with graphitic structures in char-containing ash particles. Copper acts as a catalyst for these reactions.^[54]

Studies of household waste burning indicate consistent increases in dioxin generation with increasing PVC concentrations.^[55] According to the EPA dioxin inventory, <u>landfill fires</u> are likely to represent an even larger source of dioxin to the environment. A survey of international studies consistently identifies high dioxin concentrations in areas affected by open waste burning and a study that looked at the homologue pattern found the sample with the highest dioxin concentration was "typical for the pyrolysis of PVC". Other EU studies indicate that PVC likely "accounts for the overwhelming majority of chlorine that is available for dioxin formation during landfill fires."^[55]

The next largest sources of dioxin in the EPA inventory are medical and municipal waste incinerators.^[56] Various studies have been conducted that reach contradictory results. For instance a study of commercial-scale incinerators showed no relationship between the PVC content of the waste and dioxin emissions.^{[57][58]} Other studies have shown a clear correlation between dioxin formation and chloride content and indicate that PVC is a significant contributor to the formation of both dioxin and PCB in incinerators.^{[59][60][61]}

In February 2007, the Technical and Scientific Advisory Committee of the US Green Building Council (USGBC) released its report on a PVC avoidance related materials credit for the LEED Green Building Rating system. The report concludes that "no single material shows up as the best across all the human health and environmental impact categories, nor as the worst" but that the "risk of dioxin emissions puts PVC consistently among the worst materials for human health impacts."^[62]

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In Europe the overwhelming importance of combustion conditions on dioxin formation has been established by numerous researchers. The single most important factor in forming dioxin-like compounds is the temperature of the combustion gases. Oxygen concentration also plays a major role on dioxin formation, but not the chlorine content.^[63]

The design of modern incinerators minimises PCDD/F formation by optimising the stability of the thermal process. To comply with the EU emission limit of 0.1 ng I-TEQ/m3 modern incinerators operate in conditions minimising dioxin formation and are equipped with pollution control devices which catch the low amounts produced. Recent information is showing for example that dioxin levels in populations near incinerators in Lisbon and Madeira have not risen since the plants began operating in 1999 and 2002 respectively.

Several studies have also shown that removing PVC from waste would not significantly reduce the quantity of dioxins emitted. The European Union Commission published in July 2000 a Green Paper on the Environmental Issues of PVC. "^[64] The Commission states (page 27) that it has been suggested that the reduction of the chlorine content in the waste can contribute to the reduction of dioxin formation, even though the actual mechanism is not fully understood. The influence on the reduction is also expected to be a second or third order relationship. It is most likely that the main incineration parameters, such as the temperature and the oxygen concentration, have a major influence on the dioxin formation". The Green Paper states further that at the current levels of chlorine in municipal waste, there does not seem to be a direct quantitative relationship between chlorine content and dioxin formation.

A study commissioned by the European Commission on "Life Cycle Assessment of PVC and of principal competing materials" states that "Recent studies show that the presence of PVC has no significant effect on the amount of dioxins released through incineration of plastic waste."^[65]

End-of-life

The European waste hierarchy refers to the five steps included in the article 4 of the Waste Framework Directive:^[66]

- 1. Prevention: preventing and reducing waste generation.
- 2. Reuse and preparation for reuse: giving the products a second life before they become waste.
- 3. Recycle: any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes composting and it does not include incineration.
- 4. Recovery: some waste incineration based on a political non-scientific formula^[67] that upgrades the less inefficient incinerators.
- 5. Disposal: processes to dispose of waste be it landfilling, incineration, pyrolysis, gasification and other finalist solutions. Landfill is restricted in some EU-countries through Landfill Directives and there is a debate about Incineration For example, original plastic which contains a lot of energy is just recovered in energy instead of being recycled. According to the Waste Framework Directive, the European Waste Hierarchy is legally binding except in cases that may require specific waste streams to depart from the hierarchy. This should be justified on the basis of life-cycle thinking.

The European Commission has set new rules to promote the recovery of PVC waste for use in a number of construction products. It says: "The use of recovered PVC should be encouraged in the manufacture of certain construction products because it allows the reuse of old PVC ... This avoids

PVC being discarded in landfills or incinerated causing release of carbon dioxide and cadmium in the environment".

Industry initiatives

In Europe, developments in PVC waste management have been monitored by Vinyl 2010,^[68] established in 2000. Vinyl 2010's objective was to recycle 200,000 tonnes of post-consumer PVC waste per year in Europe by the end of 2010, excluding waste streams already subject to other or more specific legislation (such as the European Directives on End-of-Life Vehicles, Packaging and Waste Electric and Electronic Equipment).

Since June 2011, it is followed by VinylPlus, a new set of targets for sustainable development.^[69] Its main target is to recycle 800,000 tonnes/year of PVC by 2020 including 100,000 tonnes of *difficult to recycle* waste. One facilitator for collection and recycling of PVC waste is Recovinyl.^[70] The reported and audited mechanically recycled PVC tonnage in 2016 was 568,695 tonnes which in 2018 had increased to 739,525 tonnes^[71]

One approach to address the problem of waste PVC is also through the process called <u>Vinyloop</u>. It is a mechanical recycling process using a solvent to separate PVC from other materials. This solvent turns in a closed loop process in which the solvent is recycled. Recycled PVC is used in place of virgin PVC in various applications: coatings for swimming pools, shoe soles, hoses, diaphragms tunnel, coated fabrics, PVC sheets.^[72] This recycled PVC's primary energy demand is 46 percent lower than conventional produced PVC. So the use of recycled material leads to a significant better <u>ecological footprint</u>. The global warming potential is 39 percent lower.^[73]

Restrictions

In November 2005 one of the largest hospital networks in the U.S., <u>Catholic Healthcare West</u>, signed a contract with B. Braun Melsungen for vinyl-free intravenous bags and tubing.^[74]

In January 2012 a major U.S. West Coast healthcare provider, <u>Kaiser Permanente</u>, announced that it will no longer buy intravenous (IV) medical equipment made with polyvinyl chloride (PVC) and DEHP (di-2-ethyl hexyl phthalate) type plasticizers.^[75]

In 1998, the U.S. Consumer Product Safety Commission (CPSC) arrived at a voluntary agreement with manufacturers to remove phthalates from PVC rattles, teethers, baby bottle nipples and pacifiers.^[76]

Vinyl gloves in medicine

Plasticized PVC is a common material for <u>medical gloves</u>. Due to vinyl gloves having less flexibility and elasticity, several guidelines recommend either <u>latex</u> or <u>nitrile</u> gloves for clinical care and procedures that require manual dexterity and/or that involve patient contact for more than a brief period.^[77] Vinyl gloves show poor resistance to many chemicals, including glutaraldehyde-based products and alcohols used in formulation of disinfectants for swabbing down work surfaces or in hand rubs.^[77] The additives in PVC are also known to cause skin reactions such as allergic contact dermatitis. These are for example the antioxidant <u>bisphenol A</u>, the biocide <u>benzisothiazolinone</u>, propylene glycol/adipate polyester and ethylhexylmaleate.^[77]

Sustainability

PVC is made from fossil fuels including natural gas. The production process also uses sodium chloride. Recycled PVC is broken down into small chips, impurities removed, and the product refined to make pure PVC. It can be recycled roughly seven times and has a lifespan of around 140 years.

In the UK, approximately 400 tonnes of PVC are recycled every month. Property owners can recycle it through nationwide collection depots. The <u>Olympic Delivery Authority</u> (ODA), for example, after initially rejecting PVC as material for different temporary venues of the <u>London Olympics 2012</u>, has reviewed its decision and developed a policy for its use.^[78] This policy highlighted that the functional properties of PVC make it the most appropriate material in certain circumstances while taking into consideration the environmental and social impacts across the whole life cycle, e.g. the rate for recycling or reuse and the percentage of recycled content. Temporary parts, like roofing covers of the <u>Olympic Stadium</u>, the <u>Water Polo Arena</u>, and the <u>Royal Artillery Barracks</u>, would be deconstructed and a part recycled in the VinyLoop process.^{[79][80]}

See also

- Chloropolymers
- Plastic pressure pipe systems
- Plastic recycling
- Polyethylene
- Polypropylene
- Polymer clay
- Polyvinyl fluoride

- Polyvinylidene chloride
- Polyvinylidene fluoride
- PVC clothing
- PVC decking
- PVC fetishism
- Vinyl roof membrane

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External links

- The European PVC Portal (European Council of Vinyl Manufacturers) (https://web.archive.org/we b/20161004023754/http://www.pvc.org/en/)
- Polyvinyl Chloride International Chemical Safety Cards—CDC/NIOSH (https://www.cdc.gov/niosh/ ipcsneng/neng1487.html)
- The Vinyl Council of Canada (http://www.plastics.ca/)
- US Vinyl Institute (https://web.archive.org/web/20160323211843/http://vinylinfo.org/vinyl-info/abou t-vinyl/)

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