



PlasticsEurope
Association of Plastics Manufacturers

*Eco-profiles of the
European Plastics Industry*

**POLYVINYLCHLORIDE (PVC)
(BULK POLYMERISATION)**

A report by

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for

The European Council of Vinyl Manufacturers
(ECVM) & **PlasticsEurope**

Data last calculated

March 2005

IMPORTANT NOTE

Before using the data contained in this report, you are strongly recommended to look at the following documents:

1. Methodology

This provides information about the analysis technique used and gives advice on the meaning of the results.

2. Data sources

This gives information about the number of plants examined, the date when the data were collected and information about up-stream operations.

In addition, you can also download data sets for most of the upstream operations used in this report. All of these documents can be found at: www.plasticseurope.org.

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CONTENTS

POLYVINYL CHLORIDE	4
STRUCTURE OF PVC.....	4
PRODUCTION METHODS.....	5
SUSPENSION POLYMERISATION.....	5
EMULSION POLYMERISATION	5
BULK OR MASS POLYMERISATION	6
USES OF PVC	6
ECOPROFILE OF BULK PVC.....	7

POLYVINYL CHLORIDE

Of all synthetic thermoplastics, polyvinyl chloride (PVC) is probably one of the polymers in modern use with the oldest pedigree. Regnault in France first produced vinyl chloride monomer in 1835 and Baumann first recorded its polymerisation in 1872 after exposing sealed tubes containing the monomer to sunlight. The earliest patents for PVC production were taken out in the USA in 1912 and pilot plants producing PVC began in Germany and the USA in the early 1930's.

Early PVC processing technology was based on established rubber moulding processes and the products that could be manufactured were limited to those using heavily plasticised polymer. The main problem was the inability to convert the polymer into usable products without severe thermal degradation because of the tendency of the polymer to de-hydrochlorinate at elevated temperatures. It was not until the discovery of suitable stabilisers that processing technology advanced to the point where the full potential of the polymer could be realised. Nowadays, by choosing suitable stabilisers and plasticisers, the polymer can be converted into a wide variety of different products as diverse as plastisols, which provide the seals in some closures, through coated fabrics used in architectural applications, films and sheets for use in packaging applications and extruded pipes and sections for use in building applications.

STRUCTURE OF PVC

PVC is a chlorinated hydrocarbon polymer. The structure is similar to that of polyethylene except that alternate carbon atoms in the main chain have one of their hydrogen atoms replaced by a chlorine atom to give the structure shown in Figure 1.

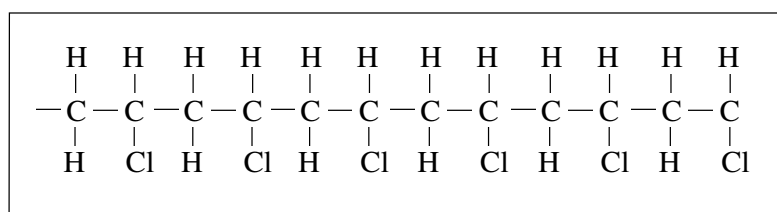


Figure 1. Structure of polyvinyl chloride

The polymer is produced from vinyl chloride by a process essentially similar to that used in the production of polyethylene, polypropylene and polystyrene; that is, the double bond in the vinyl chloride molecule is opened and neighbouring molecules combine with each other to produce a long chain molecule. Schematically the reaction is as shown in Figure 2.

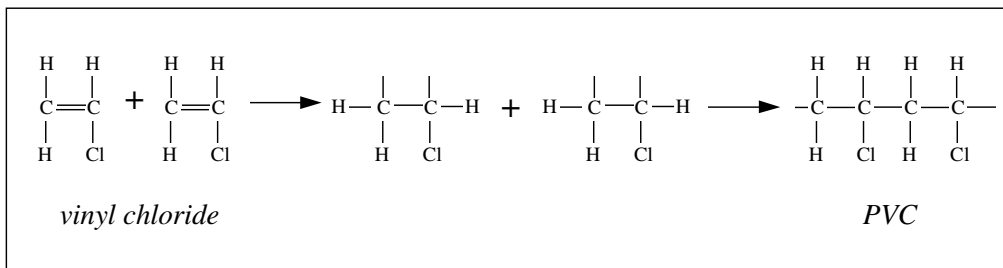


Figure 2. Schematic representation of the polymerisation of vinyl chloride.

PRODUCTION METHODS

There are three commercial processes for the production of PVC:

1. Suspension polymerisation
2. Emulsion polymerisation
3. Bulk or mass polymerisation.

Suspension polymerisation

Liquid vinyl chloride is insoluble in water and disperses to fine droplets when mechanically agitated. The droplets remain in suspension as long as the agitation continues. Polymerisation is carried out in pressurised vessels under the influence of heat and initiators and/or catalysts, which are soluble in the water. A typical initiator is an organic peroxide.

The reaction is exothermic and the heat evolved is carried to the sides of the reaction vessel by the water. Suspension agents known as protective colloids are added to the reactor to prevent the monomer droplets coalescing and the polymer particles from agglomerating.

When the desired conversion is reached, the batch is transferred to a blow down vessel. Several batches may be transferred to this vessel for blending. Unreacted monomer is recovered and recycled back to the polymerisation reactor. The polymer particles are dried.

Emulsion polymerisation

In this process, surfactants (soaps) are used to disperse the vinyl chloride monomer in water. The monomer is trapped inside soap micelles and is protected by the soap and polymerisation takes place using water soluble initiators.

The process can be either continuous or batch but both lead to a polymer latex which is a very fine suspension of polymer particles ($\sim 0.1\mu\text{m}$ diameter) in water. Excess monomer is recovered and recycled and the polymer particles are dried.

Bulk or mass polymerisation

Unlike suspension or emulsion polymerisation, bulk polymerisation is carried out in the complete absence of water, protective colloids or emulsifying agents. This process relies on the fact that the polymer is insoluble in the monomer and precipitates out to form grains that have no tendency to agglomerate. The main problem is the difficulty in heat removal and this problem is solved by carrying out the polymerisation in two stages.

In the first stage, vinyl chloride monomer is mechanically agitated in a vertical autoclave with the appropriate initiators until a conversion of 7 – 10% is achieved. This first pre-polymerisation step determines the number of particles that will be formed. Heat is removed by continuously condensing the VCM vapour above the liquid reaction mixture.

The pre-polymer is then transferred to a horizontal autoclave equipped with a slow paddle. Here, the particles already formed grow by the formation of further polymer. The process is stopped when 70 – 90% of the monomer has been converted.

Uses of PVC

Suspension PVC is the general purpose grade and is used for most rigid PVC applications such as pipes, profiles, other building materials and hard foils. It is also plasticised and used for most flexible applications such as cable insulation, soft foils and medical products.

Emulsion PVC is primarily used for coating applications such as PVC coated fabrics.

Bulk PVC is used for specific types of hard sheets and bottles.

Suspension PVC accounts for more than 80% of the PVC market. The market share for emulsion PVC is approximately 10% and for bulk PVC, 5%.

Emissions of vinyl chloride monomer and ethylene dichloride are controlled by law in several European countries. These particular emissions are dealt with in the publications *On the environmental impact of the manufacture of polyvinyl*

chloride (PVC) and ECVI Industry Charter for the Production of VCI and PVC.¹

The report is concerned with bulk or mass polymerisation.

ECOPROFILE OF BULK PVC

Table 1 shows the gross or cumulative energy to produce 1 kg of bulk PVC and Table 2 gives this same data expressed in terms of primary fuels. Table 3 shows the energy data expressed as masses of fuels. Table 4 shows the raw materials requirements and Table 5 shows the demand for water. Table 6 shows the gross air emissions and Table 7 shows the corresponding carbon dioxide equivalents of these air emissions. Table 8 shows the emissions to water. Table 9 shows the solid waste generated and Table 10 gives the solid waste in EU format.

Table 1

Gross energy required to produce 1 kg of bulk PVC. (Totals may not agree because of rounding)

Fuel type	Fuel prod'n & delivery energy (MJ)	Energy content of delivered fuel (MJ)	Energy use in transport (MJ)	Feedstock energy (MJ)	Total energy (MJ)
Electricity	12.23	5.60	0.26	-	18.08
Oil fuels	0.13	4.31	0.24	15.03	19.71
Other fuels	0.36	9.67	0.02	8.22	18.27
Totals	12.72	19.59	0.52	23.25	56.07

¹ Both of these publications are available from ECVI, Ave E Van Nieuwenhuyse 4, Box 4, B-1160 Brussels, Belgium.

Table 2

Gross primary fuels required to produce 1 kg of bulk PVC. (Totals may not agree because of rounding)

Fuel type	Fuel prod'n & delivery energy (MJ)	Energy content of delivered fuel (MJ)	Fuel use in transport (MJ)	Feedstock energy (MJ)	Total energy (MJ)
Coal	1.74	1.55	0.07	<0.01	3.36
Oil	0.58	4.50	0.32	15.03	20.43
Gas	1.13	8.08	0.07	8.20	17.48
Hydro	0.66	0.32	<0.01	-	0.98
Nuclear	8.47	4.01	0.05	-	12.53
Lignite	<0.01	<0.01	<0.01	-	<0.01
Wood	<0.01	<0.01	<0.01	<0.01	<0.01
Sulphur	<0.01	<0.01	<0.01	0.01	0.01
Biomass (solid)	0.03	0.01	<0.01	<0.01	0.05
Hydrogen	<0.01	1.13	<0.01	-	1.13
Recovered energy	<0.01	-0.06	<0.01	-	-0.06
Unspecified	<0.01	<0.01	<0.01	-	<0.01
Peat	<0.01	<0.01	<0.01	-	<0.01
Geothermal	<0.01	<0.01	<0.01	-	0.01
Solar	<0.01	<0.01	<0.01	-	<0.01
Wave/tidal	<0.01	<0.01	<0.01	-	<0.01
Biomass (liquid/gas)	0.03	0.01	<0.01	-	0.04
Industrial waste	0.01	<0.01	<0.01	-	0.01
Municipal Waste	0.05	0.02	<0.01	-	0.07
Wind	0.01	<0.01	<0.01	-	0.01
Totals	12.72	19.59	0.52	23.25	56.07

Table 3

Gross primary fuels used to produce 1 kg of bulk PVC expressed as mass.

Fuel type	Input in mg
Crude oil	450000
Gas/condensate	340000
Coal	120000
Metallurgical coal	57
Lignite	150
Peat	160
Wood	82

Table 4
Gross raw materials required to produce 1 kg of bulk PVC.

Raw material	Input in mg
Air	1300000
Animal matter	<1
Barytes	39
Bauxite	5
Bentonite	26
Biomass (including water)	9600
Calcium sulphate (CaSO ₄)	3
Chalk (CaCO ₃)	<1
Clay	1
Cr	<1
Cu	160
Dolomite	2
Fe	140
Feldspar	<1
Ferromanganese	<1
Fluorspar	4
Granite	<1
Gravel	1
Hg	<1
Limestone (CaCO ₃)	2100
Mg	<1
N ₂	45000
Ni	<1
O ₂	21000
Olivine	1
Pb	<1
Phosphate as P ₂ O ₅	<1
Potassium chloride (KCl)	280
Quartz (SiO ₂)	<1
Rutile	<1
S (bonded)	<1
S (elemental)	1500
Sand (SiO ₂)	1100
Shale	8
Sodium chloride (NaCl)	740000
Sodium nitrate (NaNO ₃)	<1
Talc	<1
Unspecified	<1
Zn	<1

Table 5
Gross water consumption required for the production of 1 kg of bulk PVC. (Totals may not agree because of rounding)

Source	Use for processing (mg)	Use for cooling (mg)	Totals (mg)
Public supply	4100000	-	4100000
River canal	610000	720000	1300000
Sea	110000	920000	1000000
Well	<1	<1	<1
Unspecified	2800000	18000000	21000000
Totals	7600000	20000000	27000000

Table 6

Gross air emissions associated with the production of 1 kg of bulk PVC. (Totals may not agree because of rounding)

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	From biomass (mg)	From fugitive (mg)	Totals (mg)
dust (PM10)	300	39	5	170	-	-	520
CO	910	270	39	220	-	-	1400
CO2	400000	640000	18000	170000	-80	-	1200000
SOX as SO2	1800	570	280	260	-	-	2900
H2S	<1	-	<1	<1	-	-	<1
mercaptan	<1	<1	<1	<1	-	-	<1
NOX as NO2	1300	950	110	1200	-	-	3500
NH3	<1	-	<1	<1	-	-	<1
Cl2	<1	<1	<1	34	-	-	34
HCl	49	3	<1	2	-	-	53
F2	<1	<1	<1	<1	-	-	<1
HF	2	<1	<1	<1	-	-	2
hydrocarbons not specified	460	40	33	630	-	<1	1200
aldehyde (-CHO)	<1	-	<1	<1	-	-	<1
organics	<1	<1	<1	48	-	-	48
Pb+compounds as Pb	<1	<1	<1	<1	-	-	<1
Hg+compounds as Hg	<1	-	<1	<1	-	-	<1
metals not specified elsewhere	<1	<1	<1	<1	-	-	1
H2SO4	<1	-	<1	<1	-	-	<1
N2O	<1	<1	<1	<1	-	-	<1
H2	35	<1	<1	240	-	-	280
dichloroethane (DCE) C2H4Cl2	<1	-	<1	27	-	<1	27
vinyl chloride monomer (VCM)	<1	-	<1	120	-	<1	120
CFC/HCFC/HFC not specified	<1	-	<1	17	-	-	17
organo-chlorine not specified	<1	-	<1	<1	-	-	<1
HCN	<1	-	<1	<1	-	-	<1
CH4	13000	140	<1	1400	-	<1	14000
aromatic HC not specified elsewhere	<1	-	<1	19	-	<1	19
polycyclic hydrocarbons (PAH)	<1	<1	<1	<1	-	-	<1
NM VOC	<1	-	<1	42	-	-	42
CS2	<1	-	<1	<1	-	-	<1
methylene chloride CH2Cl2	<1	-	<1	<1	-	-	<1
Cu+compounds as Cu	<1	<1	<1	<1	-	-	<1
As+compounds as As	-	-	-	<1	-	-	<1
Cd+compounds as Cd	<1	-	<1	<1	-	-	<1
Ag+compounds as Ag	-	-	-	<1	-	-	<1
Zn+compounds as Zn	<1	-	<1	<1	-	-	<1
Cr+compounds as Cr	<1	<1	<1	<1	-	-	<1
Se+compounds as Se	-	-	-	<1	-	-	<1
Ni+compounds as Ni	<1	<1	<1	<1	-	-	<1
Sb+compounds as Sb	-	-	<1	<1	-	-	<1
ethylene C2H4	-	-	<1	2	-	-	2
oxygen	-	-	-	<1	-	-	<1
asbestos	-	-	-	<1	-	-	<1
dioxin/furan as Teq	-	-	-	<1	-	-	<1
benzene C6H6	-	-	-	<1	-	<1	<1
toluene C7H8	-	-	-	<1	-	<1	<1
xylene C8H10	-	-	-	<1	-	<1	<1
ethylbenzene C8H10	-	-	-	<1	-	<1	<1
styrene	-	-	-	<1	-	<1	<1
propylene	-	-	-	1	-	-	1

Table 7

Carbon dioxide equivalents corresponding to the gross air emissions for the production of 1 kg of bulk PVC. (Totals may not agree because of rounding)

Type	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	From biomass (mg)	From fugitive (mg)	Totals (mg)
20 year equiv	1200000	640000	18000	270000	-80	<1	2100000
100 year equiv	690000	640000	18000	210000	-80	<1	1600000
500 year equiv	490000	640000	18000	190000	-80	<1	1300000

Table 8

Gross emissions to water arising from the production of 1 kg of bulk PVC.
(Totals may not agree because of rounding).

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	Totals (mg)
COD	1	-	<1	270	270
BOD	<1	-	<1	10	11
Pb+compounds as Pb	<1	-	<1	<1	<1
Fe+compounds as Fe	<1	-	<1	<1	<1
Na+compounds as Na	<1	-	<1	31000	31000
acid as H+	1	-	<1	18	18
NO3-	<1	-	<1	1	1
Hg+compounds as Hg	<1	-	<1	<1	<1
metals not specified elsewhere	<1	-	<1	77	78
ammonium compounds as NH4+	1	-	<1	1	2
Cl-	<1	-	<1	45000	45000
CN-	<1	-	<1	<1	<1
F-	<1	-	<1	<1	<1
S+sulphides as S	<1	-	<1	<1	<1
dissolved organics (non-	<1	-	<1	4	4
suspended solids	30	-	2	1100	1100
detergent/oil	<1	-	<1	5	5
hydrocarbons not specified	3	<1	<1	<1	3
organo-chlorine not specified	<1	-	<1	<1	<1
dissolved chlorine	<1	-	<1	<1	<1
phenols	<1	-	<1	1	1
dissolved solids not specified	<1	-	<1	3600	3600
P+compounds as P	<1	-	<1	12	12
other nitrogen as N	<1	-	<1	1	2
other organics not specified	<1	-	<1	<1	<1
SO4--	<1	-	<1	1300	1300
dichloroethane (DCE)	<1	-	<1	<1	<1
vinyl chloride monomer (VCM)	<1	-	<1	3	3
K+compounds as K	<1	-	<1	9	9
Ca+compounds as Ca	<1	-	<1	2300	2300
Mg+compounds as Mg	<1	-	<1	<1	<1
Cr+compounds as Cr	<1	-	<1	<1	<1
ClO3--	<1	-	<1	2100	2100
BrO3--	<1	-	<1	<1	<1
TOC	<1	-	<1	7	7
AOX	<1	-	<1	<1	<1
Al+compounds as Al	<1	-	<1	<1	<1
Zn+compounds as Zn	<1	-	<1	<1	<1
Cu+compounds as Cu	<1	-	<1	<1	<1
Ni+compounds as Ni	<1	-	<1	<1	<1
CO3--	-	-	<1	4900	4900
As+compounds as As	-	-	<1	<1	<1
Cd+compounds as Cd	-	-	<1	<1	<1
Mn+compounds as Mn	-	-	<1	<1	<1
organo-tin as Sn	-	-	<1	<1	<1
Sr+compounds as Sr	-	-	<1	<1	<1
organo-silicon	-	-	-	<1	<1
benzene	-	-	-	<1	<1
dioxin/furan as Teq	-	-	<1	<1	<1

Table 9

Gross solid waste associated with the production of 1 kg of bulk PVC. (Totals may not agree because of rounding)

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	Totals (mg)
Plastic containers	<1	-	<1	<1	<1
Paper	<1	-	<1	<1	<1
Plastics	<1	-	<1	210	210
Metals	<1	-	<1	<1	<1
Putrescibles	<1	-	<1	<1	<1
Unspecified refuse	520	-	<1	<1	520
Mineral waste	79	-	18	850	950
Slags & ash	7900	290	7	9900	18000
Mixed industrial	-180	-	1	420	250
Regulated chemicals	640	-	<1	440	1100
Unregulated chemicals	480	-	<1	2300	2800
Construction waste	<1	-	<1	<1	<1
Waste to incinerator	<1	-	<1	250	250
Inert chemical	350	-	<1	9600	10000
Wood waste	<1	-	<1	1	1
Wooden pallets	<1	-	<1	<1	<1
Waste to recycling	<1	-	<1	190	190
Waste returned to mine	23000	-	1	13000	36000
Tailings	1	-	1	6500	6500
Municipal solid waste	-6800	-	-	<1	-6800
Note: Negative values correspond to consumption of waste e.g. recycling or use in electricity generation.					

Table 10

Gross solid waste in EU format associated with the production of 1 kg of bulk PVC. Entries marked with an asterisk (*) are considered hazardous as defined by EU Directive 91/689/EEC

Emission	Totals (mg)
010101 metallic min'l excav'n waste	170
010102 non-metal min'l excav'n waste	23000
010306 non 010304/010305 tailings	3
010308 non-010307 powdery wastes	1
010399 unspecified met. min'l wastes	24
010408 non-010407 gravel/crushed rock	<1
010410 non-010407 powdery wastes	<1
010411 non-010407 potash/rock salt	370
010499 unsp'd non-met. waste	<1
010505*oil-bearing drilling mud/waste	610
010508 non-010504/010505 chloride mud	480
010599 unspecified drilling mud/waste	520
020107 wastes from forestry	1
050106*oil ind. oily maint'e sludges	2
050107*oil industry acid tars	100
050199 unspecified oil industry waste	100
050699 coal pyrolysis unsp'd waste	16
060101*H ₂ SO ₄ /H ₂ SO ₃ MFSU waste	4
060102*HCl MFSU waste	-1
060106*other acidic MFSU waste	<1
060199 unsp'd acid MFSU waste	<1
060204*NaOH/KOH MFSU waste	<1
060299 unsp'd base MFSU waste	<1
060313*h. metal salt/sol'n MFSU waste	7900
060314 other salt/sol'n MFSU waste	38
060399 unsp'd salt/sol'n MFSU waste	57
060404*Hg MFSU waste	16
060405*other h. metal MFSU waste	42
060499 unsp'd metallic MFSU waste	150
060602*dangerous sulphide MFSU waste	<1
060603 non-060602 sulphide MFSU waste	3
060701*halogen electrol. asbestos waste	1900
060702*Cl pr. activated C waste	<1
060703*BaSO ₄ sludge with Hg	1
060704*halogen pr. acids and sol'ns	8
060799 unsp'd halogen pr. waste	100
061002*N ind. dangerous sub. waste	<1
061099 unsp'd N industry waste	<1
070101*organic chem. aqueous washes	<1
070103*org. halogenated solv'ts/washes	<1
070107*hal'd still bottoms/residues	150
070108*other still bottoms/residues	5
070111*org. chem. dan. eff. sludge	<1
070112 non-070111 effluent sludge	<1
070199 unsp'd organic chem. waste	23
070204*polymer ind. other washes	<1
070207*polymer ind. hal'd still waste	66

continued over

Table 10 - continued

Gross solid waste in EU format associated with the production of 1 kg of bulk PVC. Entries marked with an asterisk () are considered hazardous as defined by EU Directive 91/689/EEC*

070208*polymer ind. other still waste	220
070209*polymer ind. hal'd fil. cakes	<1
070213 polymer ind. waste plastic	<1
070214*polymer ind. dan. additives	130
070216 polymer ind. silicone wastes	<1
070299 unsp'd polymer ind. waste	460
080199 unspecified paint/varnish waste	<1
100101 non-100104 ash, slag & dust	8200
100102 coal fly ash	340
100104*oil fly ash and boiler dust	<1
100105 FGD Ca-based reac. solid waste	350
100113*emulsified hyrdocarbon fly ash	<1
100114*dangerous co-incin'n ash/slag	1500
100115 non-100115 co-incin'n ash/slag	10
100116*dangerous co-incin'n fly ash	130
100199 unsp'd themal process waste	4
100202 unprocessed iron/steel slag	40
100210 iron/steel mill scales	3
100399 unspecified aluminium waste	<1
100501 primary/secondary zinc slags	<1
100504 zinc pr. other dust	<1
100511 non-100511 Zn pr. skimmings	<1
101304 lime calcin'n/hydration waste	4
130208*other engine/gear/lub. oil	<1
150101 paper and cardboard packaging	<1
150102 plastic packaging	<1
150103 wooden packaging	<1
150106 mixed packaging	<1
170107 non-170106 con'e/brick/tile mix	<1
170904 non-170901/2/3 con./dem'n waste	<1
190199 unspecified incin'n/pyro waste	<1
190905 sat./spent ion exchange resins	9600
200101 paper and cardboard	<1
200108 biodeg. kitchen/canteen waste	<1
200138 non-200137 wood	<1
200139 plastics	10
200140 metals	<1
200199 other separately coll. frac'ns	-690
200301 mixed municipal waste	1
200399 unspecified municipal wastes	-6300
Note: Negative values correspond to consumption of waste e.g. recycling or use in electricity generation.	