7.2. Physical and Chemical Properties

7.2.1. Vinyl Chloride Monomer (VCM)

Vinyl chloride monomer (VCM), *bp* −13.4 °C, is a gas at room temperature and pressure. Therefore, it is handled as a compressed volatile liquid in all polymerization operations. Its vapor pressure over the typical polymerization temperature range of 50° to 70 °C is 800 − 1250 kPa. As a result PVC polymerization reactors are thick-walled jacketed steel vessels with a pressure rating of 1725 kPa. VCM is slightly soluble in water (0.11 wt% at 20 °C). Whilst this has some influence on the suspension polymerization process it is critically important to the success of the emulsion polymerization process described in Section 7.4.3. The polymerization of VCM is strongly exothermic, and its specific heat and heat of evaporation of 1.352 $kJ\,kg^{-1}\,K^{-1}$ and 20.6 kJ/mol, respectively, allow the use of a condenser to remove the heat of reaction as well as by the more conventional jacketed vessel systems. Its explosive limits in air are 4 − 22 vol% and plant design, particularly when handling unreacted VCM in the recovery system, must be designed and operated accordingly.

7.2.2. Poly(Vinyl Chloride) (PVC)

PVC is never used alone. It is always mixed with heat stabilizers, lubricants, plasticizers, fillers, and other additives to make processing possible, all of which can influence its physical and mechanical properties. Table 1 lists properties of rigid (unplasticized) PVC with a total additives content of $<10\%$. Table 2 list properties

Table 1. Typical properties of rigid PVC (UPVC)

Property	Test	Value
Tensile strength at 23 °C, MPa	BS 2782 : 301G ISO R527	55
Tensile modulus (1 % strain, 100 s), GPa	BS 4618 ISO R899	2.7 – 3.0
Tensile modulus (1 % strain, 3 years), GPa	ISO R899	1.7
Izod impact, ft lb/in	BS 2782 : 306A ISO R180	2 (unmodified) 10 (modified)
Specific gravity	ISO R1183	1.38 – 1.45
Coefficient of linear thermal expansion, K^{-1}	BS 4618 : 3.1	6×10^{-5}
Coefficient of thermal conductivity, W/mk		0.14
Flammability (oxygen index)	ASTM D2863 (Fenimore Martin)	45
Weathering resistance		very good (especially white)
Resistance to concentrated mineral acids (at 20 °C)		excellent
Maximum continuous operating temperature	field experience	60 °C

Table 2. Typical properties of flexible PVC

Property	Test	Value
Specific gravity	ISO R1183	1.19 – 1.68
Tensile strength, MPa	BS 2782.320A	7.5 – 30
Elongation at break, %	BS 2782.320A	140 – 400
BS softness	BS 2782 365A	5 – 100
Cold flex temperature, °C	BS 2782 159B	– 20 to – 60
Volume resistivity at 23 °C, $\Omega \cdot$ cm	BS 2782 202A	$10^{10} – 10^{15}$
Ageing resistance	field experience	excellent
Ozone resistance	field experience	very good

of flexible (plasticized) PVC where the range of physical properties varies widely, depending on the plasticizer content. This can vary between 20 and 100 phr so as a guide properties typical of a plasticizer content of 50 phr are given.

In addition the K-value (molecular mass) of the PVC can also influence properties significantly (see Section 7.4.1.4.3).

PVC has extremely good chemical resistance to all but low molecular mass chlorinated solvents. Therefore, it is widely used in the construction and lining of chemical plants.

7.3. Resources and Raw Materials

VCM is produced industrially by two main reactions:

1) Hydrochlorination of acetylene
2) Thermal cracking of 1,2-dichloroethane produced by direct chlorination or oxychlorination of ethylene in the balanced process. Presently, more than 90 % of the VCM produced is based on this route.

In an ideal situation a PVC plant is fully integrated, beginning with ethylene and chlorine (salt), but various levels of integration are employed worldwide. Stand-alone PVC plants, supplied with VCM by sea, road, or rail, are well known as are ones making the bulk of their VCM requirements from scratch on site, with supplementary supplies of 1,2-dichloroethane for cracking to satisfy peak demand. Finally, there are fully integrated plants which have the benefit of uninterrupted supplies of base raw materials (ethylene and salt) and where the monomer is supplied by pipeline at a significant cost benefit. It can cost up to 120 DM/t to transport VCM within continental Western Europe depending on distance and type of freight used, i.e., road, rail or ship.

7.4. Production

There are three main processes used for the commercial production of PVC: suspension (providing 80 % of world production), emulsion (12 %) and mass, also called bulk (8 %).

7.8. Processing and End Uses

Due to its unique combination of properties PVC is never handled on its own. Instead a complex formulation incorporating several additives is used. A typical base formulation contains: PVC resin, heat stabilizer(s), internal lubricant(s), external lubricant(s), processing aid, and additionally, impact modifier, filler(s), pigment, UV stabilizer, as well as primary and secondary plasticizers.

PVC is intrinsically unstable because of molecular defects in some of the polymer chains [60], [61] and when subjected to heat they initiate a self-accelerating dehydrochlorination reaction. Stabilizers neutralize the HCl produced and introduce nucleophilic substitution reactions that prevent further degradation [60], [61]. Table 11 gives a summary of the *heat stabilizers* in regular use.

Table 12. Typical end uses for PVC

Application	Rigid PVC	Flexible PVC
Construction	window frames, gutters, pipes, cars, housesiding, ports, roofing	waterproof membranes, cable insulation, roof lining, greenhouses
Domestic	curtain rails, drawer sides, laminates, audio and video tape cases, records	flooring, wallcoverings, shower curtains, leathercloth, hosepipes
Packaging	bottles, blister packs, transparent packs and punnets	cling film
Transport	car seat backs	underseal, roof linings, leathercloth upholstery, wiring insulation, window seals, decorative trim
Medical		oxygen tents, bags and tubing for blood transfusions, drips and dialysis liquids
Clothing	safety equipment	waterproofs for fishermen and emergency services, life-jackets, shoes, wellington boots, aprons and baby pants
Others	floppy-disk covers, credit cards	conveyor belts, inflatables, sports goods, toys

The polar, highly viscous PVC melt sticks easily to metal walls of extruder barrels, calenders, mills, etc. so an *external lubricant* is employed to assist the smooth passage of the melt. *Internal lubricants* help to reduce melt viscosity and prevent overheating and so help to ensure good color of the final product. *Processing aids* improve the surface appearance of extruded sections and reduce melt defects such as screw memory, where the helical nature of the screw can be seen as regular ripples in the pipe surface. Many other additives can be used, e.g., *impact modifiers* for bottles and *UV stabilizers* and *fillers* (e.g., TiO_2) for house sidings and window frames to ensure the best possible in-service performance or longevity.

In all extrusion and some other conversion processes the PVC grain is not broken down to its constituent primary particles [62], unlike emulsion PVC processing (see Section 7.4.3.6). Instead the suspension grains (150 μm) gradually lose their original form by fusion and elongation under the influence of heat, pressure, and shear so that in badly processed PVC grain memory can be detected by optical microscopy of cross sections of extrudates [62]. In practise converters take great care to ensure that the degree of gelation (i.e., lack of grain memory) in the final PVC article is very high. Degree of gelation can be measured by determining the degree of attack by a poor solvent such as acetone or methylene chloride or by measurement of flow pressure to assess the strength and elasticity of partially fused material directly [63].

The enormous subject of processing, including different aspects such as formulations, types of processing equipment, gelation, rheology and mechanical properties is covered more widely in [62], [64]–[68].

The versatility of PVC can be gauged by the very broad summary of typical end uses given in Table 12.

Table 13. North American Producers of VCM and PVC in 1991

Producer	PVC capacity $\times 10^3$, t	VCM capacity $\times 10^3$, t
BF Goodrich	1130	610
Occidental	970	1140
Shintech	900	0
Formosa Plastics	810	550
Georgia Gulf	440	570
Vista	390	360
Borden	340	430
Pacific Western [a]	230	
Esso	130	
Certain Teed	120	
Union Carbide	60	
Vygen Corp.	60	
Keysor Corp. -	30	
Goodyear	30	
Dow		1400
PPG		360
Westlake [b]		450

[a] Ex Air Products.
[b] Ex BF Goodrich.

7.10. Toxicology and Occupational Health

Vinyl Chloride Monomer (VCM). Since vinyl chloride boils at – 13 °C it is handled as a compressed liquid. It has a vapor density greater than air so precautions are taken in design not to contain the vapor in restricted areas. Protection of reactors by relief valves or bursting disks and double-valve isolation of all lines containing VCM are basic precautions taken in the design and construction of any PVC plant vessel which contains monomer. The gas is explosive between 3.6 and 25 vol % with air and 12 vol % oxygen is required for ignition [69]. Therefore, a special series of working conditions must be satisfied in the working environment and great care is always taken to purge lines, pumps, valves, etc. before any maintenance work is started. Thorough documentation (e.g., clearance to work certificates) are always used to ensure proper isolation of plant equipment is carried out before any entry. The whole plant is contained within a "red-fence" area where smoking is not permitted and where all electrical equipment is of a gas-tight and "flame-free" construction.

VCM has a narcotic effect at 8 – 12 vol % concentration and can cause death at higher concentrations [69]. For this reason early VCM and PVC plants were designed to avoid build-up of gas above 1000 ppm in the atomosphere. VCM has a pleasant ethereal smell which is first noticed at concentrations of 500 – 2000 ppm.

Exposure to VCM has been shown to lead to two distinct problems. In the mid-1960s it became clear that a number of workers involved in reactor cleaning suffered from a bone condition called acroosteolysis (AOL), which affects mainly the hands and feet. Removal of the worker from exposure to VCM leads to an almost complete recovery. Since improvements to ventilating reactors and the introduction of high-pressure water cleaning the incidence of AOL has ceased [70]. A study of long-term exposure of rats to 30 000 ppm VCM did not reproduce any sign of AOL but they did develop cancers in various sites [71].

Subsequently, an extensive study with a wide range of dose conditions relating to occupational exposure was begun in 1971 at the Institute of Oncology in Bologna [72]. This showed that a very rare liver cancer, angiosarcoma could be formed in rats at levels of 250 – 500 ppm VCM. The first correlation between exposure to VCM and cancer in humans was made in 1973 when three workers at a plant in Louisville, Kentucky were shown to have died from angiosarcoma [73]. Since then other cases have been identified, all of which involved workers exposed to high concentrations of VCM as reactor cleaners or charging operators. As the period between first exposure to VCM and the appearance of angiosarcoma is 20 to 25 years it is likely that the incidence of the disease will soon decrease following improvements made to operation of PVC plants since 1973.

The knowledge that VCM is a human carcinogen has led to the introduction of very stringent controls by governmental and regulatory authorities to limit the exposure of workers and the general public to the monomer. In the United States, OSHA has set an 8-h TWA of 1 ppm VCM. During a shift an employee's exposure must not exceed 5 ppm over a period of 15 min or less [74]. The European regulations, EC directive 78/610, require an annual average of < 3 ppm in the plant's airspace with alarm values of 15 ppm over 1 h, 20 ppm over 20 min, and 30 ppm over 2 min.

Poly(Vinyl Chloride). Strict limits have been set for the quantity of residual VCM in processed PVC articles intended for use in food contact applications.

In 1979 the EC set an upper limit of 1.0 ppm in the article and 10 ppb in the food. In 1986 the FDA suggested levels of ≤ 5 ppb in rigid and ≤ 10 ppb in plasticized PVC articles in food contact applications. To ensure these limits are met, PVC producers aim for these concentrations in the polymer grains themselves so that any further loss during processing ensures even greater safety.

There is little evidence that PVC powder itself causes any significant medical problems but steps are always taken to reduce powder emissions because of its nuisance value.