Practical Guide to
Polyvinyl Chloride

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Contents

1 Introduction

1.1 Background

Polyvinyl chloride (PVC) is a product based on the earth's natural resources: salt and gas or oil. Salt water electrolysis yields chlorine (in addition to caustic soda and hydrogen). Ethylene can be derived from naphtha when oil is refined or from natural gas. Chlorine and ethylene can be combined to form the monomer vinyl chloride. PVC results from the polymerisation of vinyl chloride.

PVC cannot be processed on its own due to its very low thermal stability and high melt viscosity. Therefore, it is necessary to combine with the polymer a number of suitable additives to give a wide and varied range of properties to satisfy many different end-use applications. It is this scope for generating a wide range of properties through appropriate formulation that gives PVC a broad application coverage that is unmatched by any other commodity thermoplastic. Its durability (85% is used in medium- to long-term lifespan applications), linked to its cost effectiveness, has made it the second largest commodity plastic after polyethylene (PE).

PVC is a thermoplastic, meaning that it has the property of softening or fusing when heated and hardening when cooled. Thermoplastic materials, correctly formulated, can undergo this process many times without undergoing any appreciable chemical change. PVC has primarily an amorphous structure, i.e., lacking positional order on the molecular scale, and shows typical characteristics of dimensional stability up to the glass transition temperature (T_g): creep resistance, low shrinkage, impact resistance but notch sensitive, and good transparency. T_g is the temperature at which a glassy polymer, such as PVC, softens into a viscous rubbery phase, indicating when the amorphous regions gain enough thermal energy to begin sliding past one another at an observable rate. For PVC, this lies in the region of 80 °C. Being amorphous, PVC has no distinct melting point, but 170–180 °C is the temperature range at which the polymer undergoes significant change.

Although primarily amorphous, there is also a crystalline phase amounting to around 10% of the matrix.

The properties of PVC are influenced by its average molecular weight and its molecular weight distribution. PVC compounds are based on the combination of the polymer and additives that give the formulation necessary for the end use. The convention for recording the additive concentration is based on parts per hundred of the PVC resin (phr).

The compound is generated by intimately mixing together the ingredients. The mixture is subsequently converted into a gelled material under the influence of heat (and shear). Depending on the type of PVC and additives, the compound prior to gelation is normally a free-flowing powder known as a dry blend.

PVC compounds can be formulated, using plasticisers, into flexible materials, usually called PVC-P. An alternative compound form for PVC-P is a liquid in the form of a paste or liquid dispersion. Dry blend compounds without plasticiser, for rigid applications, are designated PVC-U.

1.2 History

The existence of the vinyl chloride monomer was reported by Liebig and Regnault in 1835, but the ability of this monomer to polymerise was not fully known at that time. The effect of sunlight on vinyl chloride was later investigated by Baumann in 1878, when it was observed that a tough white substance formed as a result.

Very little significant advance was then made until 1912–1916 when Fritz Klatte discovered the basis for the production of PVC. Patents were granted for the manufacture of vinyl chloride by reacting hydrogen chloride gas with acetylene at 180 °C in the presence of metal chlorides as catalysts. The patents also referred to polymerisation by sunlight and suggested some use for the polymer. The PVC patents were allowed to lapse and the first commercial production of PVC started in the late 1920s, in the USA, with expansion in the 1930s.

Pilot plant production of PVC resins began in Germany in 1931. The beginning of PVC as a technically useful product stemmed from the patent disclosures of Semon of the BF Goodrich Company and Reid of Carbide and Carbon Chemicals in 1933–1934. It was discovered that PVC became a flexible material that resembled rubber or leather when it was heated in the presence of a high-boiling-point liquid. This led to the use of phthalate esters as plasticisers for PVC giving a material that was processable at acceptable melt temperatures into products that were permanently soft and flexible.

The industrial production of PVC using emulsion and suspension technology had occurred in Germany, the USA, and the UK by the start of World War II. During the war, the acute shortage of rubber accelerated developments in this area, particularly in electrical cable insulation and sheathing.

During this period, heat stabilisers were first used in PVC formulations. In a further development during World War II, German engineers produced rigid sheet and pipe, although PVC-U was generally considered too brittle for practical use. Early PVC processing was carried out on machinery originally developed for rubber and celluloid, namely compounding, calendering, compression moulding, and extrusion.

1.3 Major Advantages and Limitations

1.3.1 Major Advantages

PVC is extremely cost effective in comparison to other plastics with a high degree of versatility in end-use and processing possibilities, as the reader will note from the following chapters. It is durable, easily maintained, and can be produced in a large range of colours. Outdoor weathering is also extremely good from suitably formulated material. Similarly, PVC can be used for food contact and medical applications. Clarity is good.

It has a good combination of stiffness (particularly at low wall thickness) and impact strength, linked to non-flammability in rigid use. The dimensional stability is also good at ambient temperatures. It has resistance to many different chemicals, oils, and greases, and also has good water vapour barrier properties. In its flexible form, it has good electrical insulation properties. It also has high strength-to-weight ratio with toughness and can be decorated with different techniques.

PVC has also been able to adapt well to changing needs and environments. The industry has also started to tackle end-of-life issues.

1.3.2 Limitations

In comparison to other thermoplastics, the specific gravity of PVC is higher and heat distortion and softening temperatures are relatively low. Continuous service temperature is also relatively low.

It is more difficult to melt process, due to thermal stability and high shear issues, e.g., injection moulding of PVC-U is not straightforward. PVC-U has limited solvent stress cracking resistance and becomes brittle at low temperatures unless impact modified.

There have been, and still are, issues and perceptions over environmental and health acceptance covering vinyl chloride monomer (VCM), dioxins, phthalate plasticisers, and lead (and cadmium) based heat stabilisers (see Chapter 9). As a result, PVC has lost market share in some consumer-driven markets where 'PVC free' has been used as a green marketing tool.

Mixed plastic waste containing PVC can cause processing problems due to thermal stability issues – so the polymer is not well regarded by some recyclers.

1.4 Applications

PVC is used in a very wide range of differing applications, ranging from short to long life. Around 60% of its applications have a lifetime of more than 40 years. Applications can be classified under the categories shown in **Table 1.1**. By far, the biggest market area is in construction (>60%).

1.5 Competitive Materials

Polyolefins are the main competitive materials for pipe, cable, and flooring, primarily due to the constant environmental pressures on PVC.

Polyethylene terephthalate (PET) has already partially replaced PVC in some rigid packaging applications. PET displays physical property similarities to PVC with a similar cost. It has superior performance in carbonated beverage bottles. The recycling of PET packaging waste is also seen to be less problematical when separated from municipal waste.

For good transparency, high impact strength, and good chemical resistance methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) copolymer, also known as transparent actylonitrile-butadiene-styrene, could be a potential higher-cost alternative for specific PVC-U areas.

1.6 Market Share and Consumption Trend

PVC vies with polypropylene (PP) to be the second largest commodity thermoplastic, in volume terms, after PE. Annual global consumption in 2002 was in excess of 25 million tonnes with the global consumption of the five major thermoplastics (polystyrene (PS) and PET being the others) at around 130 million tonnes (source: Hydro Polymers).

The global PVC market is growing at 3–4% per year, but this varies widely across the regions. Most growth is in Asia (particularly China) with the mature Western Europe market estimated to grow at around 3% per year. Eastern Europe will be higher and the North American market is still growing (source: ECVM). In 2004 production in the USA increased by 8.8% with a sales growth of 6.6% over the preceding year (American Plastics Council news release on *www.vinylinfo.org*).

Table 1.1 Typical applications of PVC (rigid and flexible)	
Construction	Window frames, doors, roller shutters, potable pressure pipe, sewage and drainage pipe, guttering, cladding, roofing membrane, cable duct and conduit, flooring, wall covering, reservoir lining, fencing, corrugated and insulation sheet, slats and blinds
Electrical	Keyboards, computers, power tools, electrical cable, telecommunication cable, duct, fuse boxes, wall plugs
Automotive	Interior trim, dashboard skin, coated fabric for seat coating and door panels, wire harness systems, window seals and gaskets, windscreen sandwich film, sealant for underbody and joints, sound insulation, decorative and protective profiles, tarpaulins
Medical	Pharmaceutical blister packs, blood and plasma bags, tubing for dialysis, endotracheal, and feeding, infusion kits, surgical and examination gloves, inhalation masks, pouches for waste products (colostomy bags, etc.)
Packaging	Food packaging: PVC-U: thermoformed blister packs/display trays/egg boxes, tamper-evident packaging, bottles for mineral water/fruit squash/cooking oils PVC-P: cling and stretch film for wrapping food products (including meat), cap seals/closures and food can linings/hose and tubing for drinks transportation
	Non-food packaging: Trays, containers, and bottles for cosmetics, medicines, and detergents, bottle cap sealing closures, adhesive tapes, shrink film
Leisure and Sports	Toys, footballs, buoyancy aids, life vests, leisure boats, garden hose, temporary structures, coated garden tool handles, gloves (garden), luggage; credit and debit cards, smart cards, identity cards
Clothing	Raincoats, shoe soles, boots, imitation leather, fashion items
Office	Office supplies, e.g., folders, ring binders, covers
Miscellaneous	Conveyor belting, polyurethane sealants (PVC component gives non-sag consistency), waterproof membranes (for road foundations and tunnels), wire fencing, furniture coating, inks, lacquers and adhesives, valves and fittings (chemical industry), gauntlet gloves, upholstery

1.7 Industry Outline and Major Suppliers

The PVC industry consists of resin producers, compounders, additive suppliers, and processors. Most processors specialise in processes linked to either PVC-U or PVC-P applications. In some cases, such as pipe and window frame manufacturing, the processed PVC is marketed directly by the processor. In other cases, the processor passes on the PVC in semi-finished form to another company for completion.

There has been much rationalisation of resin producers in the last twenty years due to consolidation transactions. The major PVC industry participants are shown in **Table 1.2** for 2003.

Table 1.2 Nameplate capacity (based on suppliers' information)			
Western Europe	kt per year	World	kt per year
EVC	1400	Shin-Etsu (Shintech)[1] – USA, Japan and W Europe	3230
SolVin	1300	Formosa – Taiwan and USA	2550
Arkema[2]	940	Oxy Vinyls – USA and Canada	2050
Vinnolit	650	EVC – W Europe	1400
Hydro Polymers	475	SolVin – W Europe	1300
Tessenderlo (LVM)	475	Georgia Gulf – USA	1220
Shin-Etsu[3]	440	LG Chem – Korea and China	1130
Vestolit	350	Arkema – W Europe	940
Cires	200	Vinnolit – W Europe	650
Aiscondel	160	Kanegafuchi – Japan	530

[1] Shin-Etsu has announced that they will build and operate an integrated facility for the manufacture of chlorine, caustic soda, VCM and PVC in the USA. PVC capacity will be 580 kt per year for completion by the end of 2007.

[2] Arkema has announced an investment plan to shut down some plants and expand others.

[3] Shin-Etsu has announced an expansion of capacity by 100 kt.

The world PVC capacity in 2003 has been estimated at around 34 million metric tonnes, a doubling of capacity in comparison to 1980. The biggest increase has been in Asia, which accounts for around 40% of the capacity. West Europe has around 20% with North America at 25%. Capacity will increase further by 2010 to approximately 40 million metric tonnes, primarily in Asia (source: CMAI).

1.8 Material Pricing

Pricing is influenced by supply chain factors, such as the supply/demand balance for ethylene dichloride (EDCL)/VCM, plant capacity utilisation, and demand in the market.

Figure 1.1 shows the average PVC price movement, for Europe, in €/tonne since February 2003.
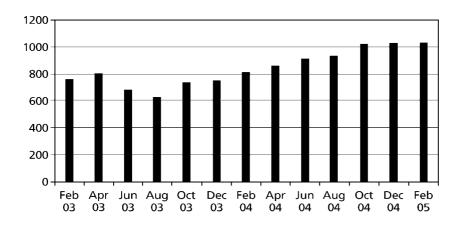
Figure 1.1 PVC price movement (€/tonne). (Source: EPN.)

The North American price for PVC (14th March 2005) was approximately US$0.57/pound (source: Plastics News, *www.plasticsnews.com*).

Table 1.3 shows a snapshot comparison of PVC with other commodity plastics.

Table 1.3 Polymer prices, February 2005 (source: EPN)	
Material	**Price (€/tonne)**
PVC pipe grade	1000–1030
PVC high-quality grade	1040–1070
High-density PE (average)	1110–1150
Linear low-density PE	1160–1190
Low-density PE	1230–1260
PP	1080–1130
PP copolymer	1130–1170
PS general purpose	1230–1270
PS high impact	1380–1420
PET	1320–1370

1.9 Safety, Health, and Environmental Issues

Safety, health, and environmental (SHE) issues have been a major concern, worldwide, for the PVC industry. Some issues have been debated and have receded into the background but others are still potential issues to be resolved. Some of the issues are covered in this section, but full information is available in Chapter 9.

1.9.1 Phthalate Plasticisers

Concerns have been raised at regular intervals in Europe and the USA regarding the possible negative impact of phthalates on the environment and human health due to alleged carcinogenic, endocrine modulating, reproductive, and other effects. In particular, their use in toys, healthcare products, and flooring has raised much debate and analysis at various levels, primarily concerning migration out of the flexible PVC. Strong viewpoints against the continuing use of phthalates have been expressed by non-governmental organisations (NGO) such as Greenpeace, Friends of the Earth, and WWF. They have also become a 'political football' at EU level.

There is an overall perception developing, linked to a lack of understanding between hazard and risk, that phthalates are not fully acceptable materials for the plasticisation of PVC.

The main phthalates under investigation are butylbenzyl phthalate (BBP), dibutyl phthalate (DBP), di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP) (see Section 3.2). These phthalates accounted for about 90% of the 900,000 tonnes of plasticisers used for PVC plasticisation in Europe in 2003. Investigations concerning phthalates include EU risk assessments based on sound science but the political positions on flexible PVC and phthalates cannot be ignored.

Hundreds of studies have been carried out on phthalates and there are regular updates on the regulatory position on various websites including those of the European Council for Plasticisers and Intermediates (*www.ecpi.org*) and the Phthalate Esters Panel of the American Chemistry Council (*www.phthalates.org*).

DINP, the most commonly used plasticiser in soft toys and items intended to be put into children's mouths, has had a positive EU and USA (Consumer Product Safety Commission) risk assessment, provided that recommended migration limits have been adhered to.

However, on the basis of the precautionary principle (see Section 9.2.3), an EU ban on the use of DEHP, DBP, and BBP in toys and babycare items was proposed in September 2004. In addition, DINP and DIDP would be banned in toys and childcare items that can be put in the mouth by children under three years old. DEHP is the only phthalate that has European Pharmacopoeia approval for flexible PVC medical devices. There has been some academic work carried out to reduce DEHP migration from flexible PVC.

1.9.2 Heat Stabilisers

1.9.2.1 Lead-based Stabilisers

Lead-based stabilisers are primarily used, extensively for PVC-U applications in Europe and the Far East, e.g., pipe, fittings and profile, lead stabilisers have been very cost-effective heat stabilisers. For similar reasons, plus good insulation resistance, lead stabilisers have also been used in PVC-P in wire and cable across the world. Their toxicity hazards have been well known and controlled, particularly in relation to worker exposure.

However, the EU hazard classification and labelling (which focuses on worker protection) of lead stabilisers as reprotoxic, harmful, dangerous for the environment, and producing dangerous cumulative effects, and their presence (heavy metal) causing issues for waste management strategies, resulted in their agreed phase-out in Europe (see Section 9.2.3.4).

A new European standard reducing the lead level in drinking water by 2013 was an additional factor (see Section 4.9.1.2).

1.9.2.2 Organotin Stabilisers

Organotin stabilisers have been caught up in the 'elimination of heavy metal' discussions. There are also improved analytical techniques now available to detect very low levels of organotin species in different environments. The identification of a perceived hazard, of course, must be related to the chance of that hazard having an effect (the risk) and this is not always appreciated.

1.9.3 Bisphenol A/Alkylphenols

Bisphenol A has been used as an inhibitor at the PVC polymerisation stage and as an antioxidant. There has been some concern over possible health hazards and its use in the polymerisation stage has been voluntarily stopped or restricted to levels that do not exceed the predicted no-effect concentration in waste water, and so on. The determination of the content of bisphenol A in, and its migration from, PVC film has been carried out [1].

Nonylphenol can be generated from some liquid heat stabilisers (in addition to many other possible sources) and it has been identified as persistent and oestrogenic [2].

1.9.4 Epoxidised Soya Bean Oil (ESBO)

ESBO is a heat stabiliser and secondary plasticiser used in PVC-P applications. It has food contact approval up to certain limits but there have been some health/political issues (see Section 9.2.3.4, subsection on epoxidised soya bean oil). The possible use of genetically modified soya bean oil in the manufacture of ESBO has also raised some discussion.

The migration of ESBO from PVC-P used in gaskets for sealing baby food jars has been determined [3].

1.9.5 Green Product Procurement Policies/Eco-labelling

As a result of the ongoing environmental debate, various organisations and local authorities have banned the use of PVC in applications where they have control of the purchasing specification, e.g., windows for local authority housing. This has been unfairly labelled under a green procurement policy.

There is a growing debate at EU and at municipality network level about the direct use of eco-labels for green public procurement (GPP). These eco-labels are managed by the EU Eco-labelling Board (comprising of 25 national competent bodies) which takes decisions about the 'ecological criteria'. Across Europe, there are several examples of discriminatory GPP measures against PVC products. The PVC industry, via the European Council of Vinyl Manufacturers (ECVM) and Vinyl 2010 (see Section 9.4), are working to counter these actions.

1.9.6 End-of-life Issues

Recycling and solid waste disposal are major issues facing the PVC industry (along with many other materials).

Incineration has issues of perception concerning dioxins and acid generation, with disposal of the furnace residue also seen to be problematical. In addition, the public perception of incineration as a means of energy recovery is not positive. The possibility of landfill disposal is also a challenge, due to concerns about potential leaching out of heavy metals and phthalates. The shortage of suitable areas for landfill generally and even more so for hazardous waste will severely restrict this disposal route in the future.

Recycling of post-consumer waste is in its infancy, as far as the polymer industry is concerned. There are many issues concerning collection, separation, and processing into suitable applications. The primary issue is, of course, the start-up costs associated with a recycling operation in comparison to current costs of virgin material processed into existing applications.

1.9.7 Fire Performance

In Section 4.6.7 mention is made of the single burning item (SBI) test method and the upcoming Euroclasses for reaction to fire performance of construction materials. These include fire growth

rates, possibly smoke growth rates, and acid fume tests. For PVC, there could be potential issues in satisfying whatever classifications are established for use in particular applications. In addition to arguing the relevancy of some of these tests, reformulation may be necessary.

References

1. J. Lopez-Cervantes and P. Paseiro-Losada, *Food Additives and Contaminants*, 2003, **20**, 6, 596.

2. *ENDS Report*, 2002, **327**, 13.

3. L. Hammarling, H. Gustavson, K. Svensson, S. Karlsson and A. Oskarsson, *Food Additives and Contaminants*, 1998, **15**, 2, 203.

2 PVC Resins

2.1 Raw Starting Materials

The starting materials for commercial polyvinyl chloride (PVC) production are ethylene and chlorine. Ethylene is derived from a cracking process involving feedstock based on oil or natural gas hydrocarbons, such as ethane, propane, or butane. The process involves catalysis at high temperatures and pressures to produce ethylene and other co-products, such as propylene and butadiene. The ethylene is further processed to separate it from the co-products.

Chlorine is manufactured industrially, in the manufacture of caustic soda, by the cell electrolysis of salt water (saturated brine). Approximately 35% of Europe's chlorine production goes into PVC production. Three different electrolysis processes are currently in use (*www.eurochlor.org*):

- Mercury cell – which uses a mercury cathode (–) along the cell bottom and titanium anodes (+) located above. The application of a direct electrical current liberates chlorine at the anode with sodium dissolving into the mercury cathode to form an amalgam. In a separate reactor, the amalgam reacts with water to produce hydrogen and caustic soda solution (50%). This regenerates the mercury, which is returned to the electrolytic cell. The process is very energy intensive and appropriate measures are necessary to protect the workforce and the environment from the effects of mercury. The current emission standard, of a maximum 2 g per tonne of capacity installed, is being met by treatment of the spent brine before discharge. However, the industry has been criticised for its poor environmental performance in the past on mercury discharge. This process was the first to be performed on an industrial scale and was the most common process in Europe. For cost and environmental issues, mercury cell operations are now being phased out.

- Diaphragm cell – which uses titanium/steel alloy anodes with a porous diaphragm, standing on an iron grid cathode, to prevent the chlorine and sodium hydroxide from remixing. Hydrogen is also liberated. The process, developed in the USA, uses less energy than the mercury cell process but, as a more dilute caustic soda solution is obtained, water evaporation (more energy) is necessary to concentrate the solution. Unreacted salt also has to be removed. The process is used more widely in the USA where energy costs have been lower than in the EU. The diaphragm was originally asbestos based, with a short lifetime, which resulted in the need to dispose of large quantities of asbestos. The asbestos is now being replaced by longer life polymers.

- Membrane cell – where the cell is divided into two compartments by a membrane acting as an ion exchanger. The anodic compartment contains a saturated sodium chloride brine solution and the cathodic compartment contains water. The process is similar to the diaphragm process but the ion-selective polymer membrane only allows the sodium cations to pass through. At the negatively charged cathode, the hydrogen ions, in the water, are reduced to hydrogen gas. At the positively charged anode, chloride ions are oxidised to chlorine gas. The sodium cations flow through the membrane to form sodium hydroxide with the hydroxyl ions remaining after removal of the hydrogen ions. Energy consumption is similar to the diaphragm cells giving very pure sodium hydroxide with negligible environmental impact.

The overall reaction process for diaphragm and membrane cells is:

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2$$

The European chlorine industry is in discussions with the EU regarding sustainable development issues, including voluntary agreements covering energy efficiency optimisation, minimisation of water use, emissions reduction, optimisation of hydrogen use, and the safe transportation of chlorine (see Section 9.2.1).

2.2 Vinyl Chloride Manufacture

Vinyl chloride monomer (VCM) is produced from the direct chlorination of ethylene, using a catalyst, with pyrolysis of the resulting ethylene dichloride (or 1,2-dichloroethane; EDCL) in a cracking unit. An oxychlorination unit, in which recycled hydrogen chloride is reacted with further ethylene feedstock in the presence of catalyst and oxygen, is also employed to generate further quantities of EDCL while excess hydrogen is oxidised to form water. The integrated operation combines these three reaction steps such that vinyl chloride is made from chlorine, ethylene, and oxygen:

- Direct chlorination to EDCL: $CH_2=CH_2$ (ethylene) + Cl_2 (chlorine) $\rightarrow CH_2ClCH_2Cl$ (EDCL)

- Oxychlorination to EDCL: $CH_2=CH_2 + 2HCl + \frac{1}{2}O_2 \rightarrow CH_2ClCH_2Cl + H_2O$

EDCL is liquid at room temperature and normal atmospheric pressure. Transportation is relatively straightforward.

- EDCL cracking (thermal decomposition at high pressure and high temperature): $CH_2ClCH_2Cl \rightarrow CH_2=CHCl$ (vinyl chloride) + HCl (hydrochloric acid)

The process also includes VCM and EDCL purification stages and a by-product separation and disposal stage. A by-product of the EDCL cracking phase is acetylene due to the EDCL cracking all the way. Consequently, the HCl recycle stream is usually passed through a hydrogenation reactor to convert it back to ethylene. This in turn produces more EDCL.

A new patented technology, based on ethane-to-VCM, is also being developed by EVC International NV. The process is based on ethane (which is much cheaper than ethylene) reacting with HCl or chlorinated hydrocarbons and oxygen using a novel catalyst system.

VCM boils at –13.4 °C and is normally stored and shipped as a liquid under pressure. It forms explosive mixtures with air and is toxic (carcinogen).

2.3 Polymerisation

PVC plants can be fully integrated (the preferred option), but various levels of integration also exist in relation to being supplied with VCM and/or EDCL.

Polymerisation is based on the free radical polymerisation of VCM using initiators, such as organic peroxides, in thick-walled, high-pressure-rated steel vessels. The reaction is strongly exothermic requiring the vessels to be jacketed and the use of a condenser to remove the heat of reaction. The choice of polymerisation method depends on the ultimate application and the economics of the process.

A broad range of peroxide types are available and are typically classified by one hour half-life temperatures of between 40 and 90 °C. The initiator controls the flux of radicals and this determines the VCM polymerisation rate. The initiator type or types are chosen to suit the particular PVC grade to be manufactured. Normally supplied in aqueous suspensions or emulsions, the concentration can range from 0.05 to 0.15%. The molecular weight is generally controlled by the reaction time and temperature. Stirring conditions also influence the process.

European Council of Vinyl Manufacturers (ECVM) member companies have agreed voluntary charters covering environmental standards relating to VCM and PVC production. These are covered in Section 9.2.2.

2.3.1 Homopolymers

After polymerisation, the VCM repeat unit is linked in a head-to-tail fashion with the number of units ranging between 500 and 1500. This corresponds to a theoretical molecular weight range of approximately 40,000–170,000. The properties of PVC are influenced by the average molecular weight and the molecular weight distribution (MWD).

The chemical structure deviates from the theoretical chain with chain branching occurring during polymerisation. Details are given in Section 3.1.

Commercial PVC polymers are essentially amorphous but also have a crystalline phase amounting to approximately 10% and a two-dimensionally ordered nematic phase depending on the processing history.

The glass transition temperature (T_g) of PVC homopolymers lies in the region of 80 °C.

2.3.1.1 Suspension Polymerisation Process

Suspension-polymerised PVC (S-PVC) is manufactured when VCM is polymerised in large-scale batch reactors (autoclaves) in the presence of water, initiators (organic peroxides) that are soluble in VCM, and a protective colloid/suspending agent (e.g., polyvinyl alcohols) to stabilise the suspension. Other additives are chain-transfer/chain-extending and chain-terminating agents, antioxidants, pH regulators, and anti-foaming agents. Depending on the dosage and nature of the protective colloid and the stirring conditions, the monomer droplets can agglomerate to a greater or lesser extent in the course of the polymerisation. The reaction can be chemically short-stopped when the desired conversion has been reached. The reaction is normally allowed to run until about 90% of the VCM has been polymerised.

The suspended droplets of liquid monomer are progressively converted to solid or porous PVC particles which are insoluble in the monomer. Unreacted VCM is stripped from the polymer and recycled. The water is separated by centrifuging. The polymer is then dried, typically in fluidised bed drying equipment. Prior to the start-up of the next polymerisation cycle, the reactor is cleaned and coated with an anti-fouling agent.

The typical mean particle (grain) size of S-PVC is 100–180 μm with a range of 50–250 μm. The particles are complex and irregular in shape with a dense semi-permeable skin.

S-PVC is the most common type of resin (around 80% of total PVC produced worldwide) used in both rigid and flexible applications and grades are formulated to meet an extensive range of requirements, such as high plasticiser absorption for flexible products, or high bulk density and good powder flow required for rigid extrusion. Grades are available from a K value (molecular mass) of 50 up to 80.

2.3.1.2 Microsuspension Polymerisation Process

Microsuspension PVC is produced when VCM is mixed in a vessel with water, an initiator soluble in VCM, and an emulsifier. These components are circulated through a mixing pump (homogeniser) which causes the mixture to disperse into very fine droplets, before being placed in an autoclave. The droplets are coated with surfactant which stabilises them during the reaction. Initiation and polymerisation occur within the droplets. After polymerisation, the autoclave contains a stable dispersion of fine particles of PVC in water. As the name of the process implies, the PVC particle diameter is smaller, within the range 0.2–3 μm. Porosity is very low.

After the production of polymer, the subsequent operations for obtaining the final product are similar to those of the emulsion polymerisation process.

Microsuspension-polymerised PVC is used for producing plastisols and paste in combination with emulsion-polymerised PVC.

2.3.1.3 Emulsion Polymerisation Process

Emulsion-polymerised PVC (E-PVC) is produced in an autoclave when VCM is polymerised in the presence of water, a water-soluble initiator (peroxosulfate, and so on), and an emulsifier (anionic surfactants). The addition of copper or iron can also be used to increase the decomposition rate of the initiator (redox catalyst). At the end of the polymerisation stage, the autoclave contains a stable dispersion of fine PVC particles in water. Non-ionic surfactants can be added at this stage. From this milky emulsion (latex), the PVC is separated from the water by evaporation in spray drying equipment. A milling process follows to modify the agglomerate size before final size classification.

As the resin retains most of the emulsifiers used during polymerisation, special properties, such as improved thermal stability and greater ease of processing, are conferred on the polymer.

A larger elementary particle size can be achieved by seeding the initial emulsion system. PVC polymer latex is introduced and the particles of the new polymer grow on the seed.

The process can be in batches, semi-continuous, with the monomer added in stages, or a continuous emulsion polymerisation process with monomer and other ingredients continuously fed into the reactor and the latex withdrawn from the bottom.

The primary particles are solid, smooth-surfaced spheres which are clustered into irregularly shaped aggregates after drying, with a typical particle size of 5.50 μm. When broken down in the paste mixing process (see Section 6.2), the particle size is in the region of 0.5 μm with a range of 0.1–3.0 μm.

When E-PVC resins are mixed with a liquid plasticiser, a paste (or plastisol) is produced due to the surfactant layer around the grain surface preventing plasticiser adsorption at room temperature. Consequently these resins are called paste resins which are used in a wide range of speciality applications such as coating, dipping, or spreading. Resins are available for differing viscosity and flow requirements, speed of gelation, clarity, and gloss level. K values range between 60 and 82.

E-PVC and microsuspension-polymerised PVC account for around 10% of total PVC produced. They are also known as dispersion resins.

2.3.1.4 Mass or Bulk Polymerisation Process

In this process, the polymer is polymerised in the absence of a carrier, such as water. The mass (or bulk) polymerisation of VCM is carried out by a two-stage process. In the first stage (prepolymeriser) vigorous agitation is necessary to obtain the desired particle size distribution. Monomer and initiator are charged and polymerisation proceeds to about 10% conversion at which time the formed particles are dispersed in the bulk of the VCM. In the second stage (polymeriser) this material is slowly agitated and additional monomer and initiator are added. Polymerisation continues to approximately 20% conversion at which time all of the liquid VCM is absorbed into the porous structure of the grains leaving only dry powder. Polymerisation continues to 70–90% conversion and the unreacted monomer is recovered.

Particle size and range are similar to suspension polymer but the particles have highly spherical shapes, with higher bulk density and porosity. The heat stability and fusion properties are superior. Particular uses for this material are linked to high transparency and good plasticising properties.

The cost benefits of this process (no drying stage) are offset to some extent by difficulties in removing VCM traces from the polymer and the level of oversized material that is generated.

The number of suppliers offering PVC produced by this process is restricted to licensees of the original Pechiney St Gobain (now Arkema – formally Atofina) technology, and accounts for <10% of world PVC production.

2.3.1.5 Structure and Stability

Commercially produced PVC is inherently thermally unstable, due to some chain branching during polymerisation. Hence a heat stabiliser system is essential. The degradation process is shown in **Figure 2.1**. This reaction leads to polymer molecules with conjugated polyene sequences of 2–25 double bonds. Polymer discolouration occurs from seven double bonds onwards, starting with yellowing and deteriorating to brown and black. Subsequent secondary reactions, if not prevented, lead to chain scission and crosslinking.

2.3.2 Copolymers and Terpolymers

A number of commercial vinyl chloride copolymers are predominantly made up of VCM units with comonomer units randomly distributed in minor proportions. The suspension polymerisation process is normally used.

Grafted copolymers obtained by vinyl chloride polymerisation and polyacrylic elastomer grafting give high bulk density resins for products with high impact strength suitable for outdoor applications. The separate addition of acrylate impact modifiers to the PVC formulation is covered in Section.3.3.

A vinyl chloride – ethylene–vinyl acetate (EVA) terpolymer system also gives products with superior impact strength suitable for outdoor environments. The modifier component is a 45% vinyl acetate EVA copolymer with PVC grafted on it. EVA modification depends on a network structure.

Figure 2.1 PVC structure and degradation process

Vinyl chloride–vinyl acetate copolymers are produced containing 5–15% of vinyl acetate. These materials, having a lower T_g, can be processed at considerably lower temperatures and are particularly suited for thermoforming. Finished products are highly transparent. These grades are the basis of so-called vinyl records.

2.3.3 Chlorinated PVC (C-PVC)

C-PVC is manufactured by chlorination of PVC polymer thereby raising the chlorine content from 56% to around 66%. Chlorination takes place primarily at the CH_2 groups along the polymer chain so that the resulting structure becomes virtually a copolymer of vinyl chloride with 1,2-dichloroethylene.

Chlorination of PVC reduces the forces of attraction between the molecular chains. C-PVC is also essentially amorphous. Both of these factors allow C-PVC to be stretched more easily and to a greater extent than PVC above its T_g,. C-PVC has a T_g, approximately 50% higher than PVC but also has a higher melt viscosity in processing. The upper service temperature for C-PVC is approximately 100 °C in comparison to that of PVC at 60 °C. The number of C-PVC suppliers is very limited.

2.4 PVC Resin Characterisation

2.4.1 Molecular Weight

PVC resins are polymerised to different molecular weights to suit the particular processing technique and end-use application requirements. The resin contains a random distribution of molecular weights and therefore number-average molecular weight (M_n) and weight-average molecular weight (M_w) can be measured by various techniques. M_n is the arithmetic mean, representing the total weight of the molecules present, divided by the total number of molecules. M_w emphasises the mass of the molecules, so that the contributions of molecules, according to their size, are more significant. The MWD, which is M_w divided by M_n is a measure of the polydispersity of a polymer mixture, i.e., how widely distributed the range of molecular weights are in the mixture. Obviously, a ratio of ~1.0 indicates that the molecular weight range is narrow.

Normally, however, for production control, the dilute solution (1% in cyclohexanone at 30 °C) viscosity of the resin is used and the average molecular weight can be calculated from the Mark–Houwink–Sakurada equation expressed in terms of the Fikentscher K value or viscosity number (DIN EN ISO 1628-2E [1]/ISO 1628-2 [2]). Commercially available PVC grades are supplied in Europe with K values ranging from 50 to 80.

In the USA the molecular weight is expressed as inherent viscosity; the higher the inherent viscosity, the higher the molecular weight. The inherent viscosity or logarithmic viscosity number (η_{inh}) is expressed in decilitres per gram. Therefore, commercial PVC resins are available with an inherent viscosity range of 0.50 to 1.15 (K value 47 to 76). In Asia the polymerisation degree (according to JIS K-6720 and JIS K-6720-2 [3]) is used. Polymerisation degree figures from 600 to 1810 cover K values of 55 to 80.

2.4.2 Particle Size

The PVC particle size range and distribution influences bulk handling and processing characteristics. Various techniques can be utilised to measure particle size and range including sedimentation and optical and electrical sensing. However, sieve analysis is the most common technique quoted on data sheets. Different grades of suspension resins give percentage retention, on a 0.063 mm sieve, in the region of 90–95% and on a 0.250 mm sieve, around 1–5%. This technique can be used to measure particles above 30 μm (0.030 mm) in size and is based on a water method (ISO 1624 [4]).

Microsuspension and emulsion grades give very low retention figures on 0.125 mm (0.20%) sieve size with a mechanical flushing sieve test method (ISO 787-18 [5]). Where the alternative ISO 1624 test method is used, very low retention figures over 0.063 mm (1.0%) and 0.106 mm (0.05%) sieve sizes are typical.

2.4.3 Bulk Powder Properties

Apparent bulk density and packed bulk (or tapped) density are important properties. The bulk density determines the weight of resin that can be stored in a vessel and the amount a mixer can hold. It also has a major influence on extruder output rates. The bulk density of a resin depends upon its morphology, particle structure, and particle size distribution. For suspension resins, bulk density is typically in the range 450–550 kg/m^3 for grades designed for plasticised applications and 550–650 kg/m^3 for rigid applications - ASTM D1895-96 [6] applies.

The packed density is based on the ability of the resin to occupy the smallest space without physical distortion and is usually 10–30% greater than the bulk density.

Another important consideration is powder flow time, as it governs the speed and ease of polymer discharge from a silo or from a mixer. This is influenced by the PVC particle shape, size distribution, and compound formulation ingredients.

2.4.4 Porosity

Porosity is an indicator of free space in a PVC grain and the ability of the grain to absorb plasticiser. High porosity is obviously desirable for flexible applications requiring high plasticiser loads. For rigid applications, a certain porosity level is necessary to absorb additives. Porosity can be assessed by different test methods. The determination of plasticiser absorption, at room temperature, is carried out using a centrifugal technique (ISO 4608 [7]/ASTM D3367-98 [8]) using di-2-ethylhexyl phthalate (DEHP) as the plasticiser. Plasticiser absorption figures in the region of 25–35% are typical for S-PVC grades for flexible applications. Correspondingly, this test gives figures in the region 15–20% for S-PVC grades for rigid applications.

The determination of hot plasticiser absorption, for testing PVC pastes (ISO 4612 [9]), utilises a laboratory planetary mixer linked to torque measurement (Brabender®) where the difference in time between the plasticiser input and the dry point (where the torque starts to increase) is measured.

2.5 Storage and Transportation

Storage and transportation in bulk (as compared to 25 kg bags on pallets) is the most popular form of handling of PVC resin. Road tankers of 20 tonnes capacity are common. Big bags, made of woven polypropylene (PP), are used for 1 tonne lots.

2.6 Role of Additives

PVC formulations can include many different types of additives that assist in imparting a large range of physical and chemical characteristics. This versatility is the main reason why PVC has been so

successful as a commodity thermoplastic, from medical applications such as tubing and blood bags to long-life applications such as window frames and rainwater goods. The unique polar characteristics of PVC permit a wide range of appropriate additives to be incorporated within the polymer. The various factors that can be influenced are shown in **Table 2.1** and depend on the particular end use.

Table 2.1 Formulation factors
Cost efficiency
Process characteristics/output
Reprocessability/recycling
Clarity level
Density
Surface finish – gloss to matt
Light stability/weathering
Softness/hardness
Flexibility/stiffness
Fire properties
Electrical properties
Post-processing treatment
Impact strength – ductile/brittle
Chemical resistance
Colour
End-use legislative requirements
Operating temperature environment

2.7 Identification

The classic test for identifying PVC is to carefully apply a small flame and observe the flame colour and generated odours. Unplasticised-PVC (PVC-U) burns with a greenish-edged flame and there is a smell of hydrochloric acid. There may be some sputtering and removal of the flame source will result in the PVC flame extinguishing. Plasticised-PVC (PVC-P) will behave similarly, but may continue burning. The plasticiser smell will also become more evident.

Density is also higher than most other plastics and this can be utilised in water flotation testing (to determine if it sinks). However, it should be noted that acrylonitrile–butadiene–styrene and polycarbonate have similar densities.

The surface of the material may also assist in identification, with PVC-U being horn like and without a waxy feel, such as for PP or polyethylene.

More scientific analytical tests are based on the identification of various components [10]. Infrared spectroscopy can be used to carry out an analysis (by noting the wavelengths that the substance absorbs) and identify the material by reference to a standards database. One approach is to press a

thin film of the sample using a temperature above its glass transition temperature and to record a transmission spectrum. Alternatively, the sample could be dissolved in tetrahydrofuran, the resulting solution cast into a film, and dried prior to generating the transmission spectrum. With PVC-P, a certain amount of preparation work is required to effectively remove the interference of the plasticiser. This involves a solvent (methanol) extraction to remove the organic species.

Pyrolysis gas chromatography (GC) can also be used to generate a pyrogram which can be compared to reference standards. This involves thermal decomposition of the polymer and analysing the thermal decomposition products using GC. The GC process separates the organic compounds, due to differences in their partitioning behaviour between the mobile gas phase and the stationary phase, in a separation column. The principal diagnostic pyrolysis species from PVC are hydrogen chloride, benzene, and chlorobenzenes.

Metal stabilisation components, such as lead, barium, tin, or zinc, can also be an indication that the polymer is PVC. X-ray fluorescence spectroscopy is a common technique which operates on the basis of analysing the emission spectrum generated when an atom is externally excited. The X-rays irradiate the sample, which then emits fluorescent X-ray radiation, which is characteristic of each element present. Measurement of the intensity of the emitted energy will also indicate the amount present in the sample. This technique can also be used to measure the calcium content, i.e., filler.

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3 PVC Additives

The main groups of additives are listed in **Table 3.1** and the description of their activity should be self-evident.

Table 3.1 Additives
Heat stabiliser
Plasticiser
Impact modifier
Process aid
Lubricant
Filler
Flame retardant/smoke suppressant
Pigment
Blowing agent
Biocide
Viscosity modifier
Antistatic agent
Antioxidant
Ultraviolet absorber
Antifogging agent
Bonding agent

3.1 Heat Stabilisers [1]

As already explained in Section 2.3.1, commercially produced polyvinyl chloride (PVC) is inherently thermally unstable, due to structural defects formed during polymerisation and during processing. The degradation process has already been shown in Section 2.3.1.5 with the labile Cl* atoms being the initiation sites of PVC heat degradation. Examples of structure defects are shown in **Figure 3.1**. Other examples of initiation sites are the 2,4-dichlorobutyl branches and the presence of peroxy groups, and so on.

Heat stabilisers retard dehydrochlorination and autoxidation and reduce fragmentation. In addition, they cure existing damage. They also help to maintain light stability during use.

The thermal degradation process can be followed by analysis of the colour generated in a static or dynamic environment, usually with reference to a standard. Alternatively, heat stability can be measured on a time basis, based on hydrogen chloride (HCl) evolution.

CR$_3$

CH$_2$

CH$_2$——C——CH$_2$ Tertiary chlorine structural irregularity

Cl

Cl

CH$_2$——C——CH=CH——C——CH$_2$ Keto allylic structures generated by
thermooxidative processes

O

Figure 3.1 PVC structure defects.

The role of the heat stabiliser can be summarised as follows:

• Substitute structural defects for more stable groups.

• Stop the dehydrochlorination zipper effect by substituting the allylic chloride formed during degradation.

• Scavenge evolved HCl which has a prodegradant effect.

• React with free radicals formed (antioxidant) to avoid discoloration and crosslinking by thermal, high-stress, or photochemical processes.

• May provide lubrication.

There are many different types of heat stabilisers based on different metal salts or soaps, acting synergistically, for PVC. These are covered in the following sections.

3.1.1 Solid Form

3.1.1.1 Lead Stabilisers

Lead compounds, usually based on a mixture of lead salts, e.g., tribasic lead sulfate ($3PbO \cdot PbSO_4 \cdot H_2O$) or dibasic lead phosphite ($2PbO \cdot PbHPO_3 \cdot \frac{1}{2}H_2O$), and lead soaps with some lubricating action, dibasic lead stearate ($2PbO \cdot Pb(C_{17}H_{35}COO)_2$) or normal lead stearate ($Pb(C_{17}H_{35}COO)_2$), have been very cost-effective heat stabilisers for many years. They primarily function as very efficient HCl absorbers. Dibasic lead phosphite is also a very effective light stabiliser. They are particularly suitable for wire and cable electrical insulation because of their complete non-conductivity and the inert nature of the chlorides formed with HCl.

Technical limitations to their use have been opacity and sulfur staining. Their cumulative toxicity has been mainly concerned with worker exposure and consequently they have been heavily regulated. Apart from wire and cable, their use has been restricted to unplasticised-PVC (PVC-U) applications in Europe and Asia. North America has never accepted lead compounds in PVC-U applications, preferring the use of organotin compounds. This is covered later in Section 3.1.2.1.

Non- or low-dusting products, which include the lead components in a safe handling state, in combination with lubricants (one-pack), have been available for many years in different product forms: flake, granule, tablet, and dosage packs. These one-packs are tailored to suit the processing technique, primarily extrusion and injection moulding, and end-use specification.

However, the EU hazard and labelling classification of lead stabilisers as reprotoxic with possible risk of impaired fertility and dangerous for the environment, in addition to their harmful and dangerous cumulative effects has resulted in their agreed phase-out in Europe (see Section 9.2.3.4). Another complicating factor is their presence (heavy metal) causing issues for waste management strategies.

A new UK standard reducing the lead level in drinking water between 2003 and 2013 was an additional factor.

3.1.1.2 Calcium Zinc-based Stabilisers (Ca Zn) [2]

One of the most successful developments in recent years has been the progress made in solid Ca Zn stabiliser formulations to replace lead on a cost-effective basis. It has also been important that the components of these systems have a satisfactory low-toxicity profile.

Ca Zn formulations are a complex blend consisting primarily of:

- Calcium soap (stearate or laurate)

- Zinc soap (stearate or laurate)

- Acid scavengers such as a hydrotalcite, zeolite, and metal oxides/hydroxides

- Organic co-stabilisers such as the diketone stearoyl benzoylmethane

- Antioxidant

- Polyols, and so on.

Calcium stearate acts as an acid acceptor in addition to providing lubrication.

Zinc stearate is used to improve initial and early colour, in combination with the co-stabiliser. This functions by the co-stabiliser complexing the zinc stearate and so preventing the early formation of zinc chloride, which is a prodegradant. It should also be noted that PVC resins may react differently in the presence of zinc (zinc sensitive) and this has an influence on stabiliser formulations.

Synthetic hydrotalcites and zeolites (already used in other industries) have been developed for use in PVC stabilisation. These form addition complexes at degrading sites. Such sites tend to be deactivated and the catalytic and highly mobile HCl captured before elimination of further HCl. Hydrotalcites have a layer structure based on magnesium aluminium hydroxycarbonates containing exchangeable anions. Zeolites are crystalline sodium aluminosilicates with a cubic crystal structure of zeolite A. They are microporous with uniform pores and a high internal surface area.

Antioxidants are included at very low levels to inhibit the oxidation of the polymer matrix arising not only from thermal processing but also from subsequent photochemical and environmental influences.

Various Ca Zn-based systems, usually supplied as a one-pack including lubricants, are now available to suit the different heat stability and rheology requirements for pipe, fittings, profile, and wire and cable applications. Non-dusting product forms have also been developed, due to the light and fluffy nature of the Ca Zn soaps (stearates). Typical addition levels for Ca Zn one-packs range from 2.0 to 4.0 phr.

Solid Ca Zn systems have also been developed for plasticised-PVC (PVC-P) applications as replacements for liquid Ba Zn stabilisers where volatility and emissions may be an issue at the processing and end-use stages. Specific Ca/Zn systems are also available for food contact and medical use meeting the strict regulations that these materials have to satisfy.

Calcium and zinc are essential to life at low doses. The recommended daily intake for zinc is approximately 15 mg for adults. At high doses, toxic effects are observable. Zinc stearate is under review, under the EU Existing Chemicals Directive (see Section 9.2.3.4, subsection on zinc risk assessment).

3.1.1.3 Calcium Organic-based Stabilisers

Another major development has been the replacement of zinc with a specific organic co-stabiliser that does not rely on zinc to generate good initial and early colour. The performance of the patented uracil co-stabiliser is linked to the efficiency of conjugation and electron transfer to retard dehydrochlorination and shorten polyene sequences. Zinc-free stabilisers are claimed to have a better processing window (no influence from zinc sensitivity) than Ca Zn, although initially there were also some mistaken perceptions about zinc being a 'heavy metal'. Organic-based systems have been developed as lead replacements for rigid pipe and pipe fittings.

3.1.2 Liquid Stabilisers

3.1.2.1 Organotin Compounds

Organotin compounds are primarily based on methyl, butyl, or octyl derivatives, usually mixtures of dialkyl and monoalkyl, bound to the tin atom through a covalent C–Sn bond. Taking up the other positions are high molecular weight, highly ionic organic groups linked through a sulfur atom (mercaptide) or oxygen atom (carboxylate). The general formula is R_xSnL_{4-x}.

Tin Mercaptides

R can be methyl, butyl, or octyl (mono- or dialkylation). L is 2-ethyhexyl thioglycolate (as used in rigid bottles and films) or 2-mercaptoethyloleate (reverse ester).

The performance of organotin mercaptides is not only based on the tin metal content, but on the organotin species, mercaptide ligand chemistry, and organic co-stabiliser. In North America, the use of lower cost, reverse ester thiotins is common for PVC-U applications covering pipe, profile and sidings, and foam.

Tin, acting as a base, reacts with the HCl initially released during PVC processing (the base strength being such so as not to extract HCl from the PVC). The monoalkyltin mercaptide acts quickly to react with the labile chlorine to generate the corresponding trichloride which can further catalyse decomposition. The dialkyltin mercaptide neutralises this compound and the resulting dichloride does not catalyse any further decomposition, and also reactivates the mono-stabiliser. In addition the organotin mercaptide stabilisers are very effective antioxidants. Addition levels are 0.5–1.5 phr.

The main features of tin mercaptide stabilisers are that they provide good initial and long-term colour hold coupled with excellent clarity, linked to their good compatibility (due to high molecular weights and ester function in the mercaptan ligands).

The methyl and octyl versions are approved (up to a maximum level) for use in rigid food contact and medical applications. Limitations to their use include their relatively high cost and unpleasant odour and their use is now almost exclusively in PVC-U applications.

Tin Carboxylates

R is predominantly butyl (dialkylation). L is alkyl maleate or laurate.

Organotin maleates are relatively less efficient than the tin mercaptides but have superior light stability due to the presence of the maleic acid structure which is able to react with conjugated double bonds (Diels–Alder reaction). They usually also contain antioxidants at a low level. Addition levels are 1.5–3.0 phr. They require particular lubrication systems due to their anti-lubricating effect.

In Europe, the annual production of tin mercaptides and carboxylates has remained fairly static around the 14 kt level (*www.vinyl2010.org*). This primarily reflects an effective decrease of PVC use in packaging.

3.1.2.2 Mixed Metal Compounds

Liquid mixed metal stabilisers are used almost exclusively in PVC-P applications. The stabilisers are formulated to suit specific requirements, such as clarity, good initial colour, long-term stability, compatibility with filled, pigmented systems, and suitability for post-processing techniques. Usually a good compromise of all the necessary requirements is achieved, but specific stabiliser formulations are designed to meet one or two specific needs.

Liquid mixed metal heat stabilisers are blends of metal soaps or salts, in combination with organophosphite esters and co-stabilisers in a liquid medium. The soaps or salts can be ethylhexanoate, nonylphenate, *para-tert*-butylbenzoate, oleate, and so on.

Aryl-alkyl or alkyl organophosphites are liquid esters, which replace the labile chlorine (particularly in the presence of zinc), scavenge HCl, decompose peroxides, and act as complex Lewis acids (by accepting electron pairs). They also assist in the solubilisation of the stabiliser components.

Manufacture is based on *in situ* reaction of the metal oxides or hydroxides with the appropriate acid components. In addition to cost performance criteria, important aspects are storage stability, easy handling, and low odour.

Strongly basic carboxylates, derived from barium or calcium, are mostly HCl scavengers. Zinc and cadmium carboxylates are also able to scavenge HCl, but also substitute the allylic chlorine atoms. The

synergism between the two types is attributed to a fast exchange reaction between zinc or cadmium chloride and barium or calcium carboxylates. These reactions regenerate the active zinc (or cadmium) carboxylate and also avoid the catalytic effect in PVC degradation of zinc (or cadmium) chlorides.

Epoxidised soyabean oil (ESBO) or octyl epoxy stearate at 2.0–5.0 phr is normally also included in PVC-P formulations. This is a secondary stabiliser/plasticiser which acts as an HCl scavenger.

One issue with liquid stabilisers is the emission of volatile components (phenol from the organophosphite, solvent from the liquid dispersion medium, and so on) during processing and from the end-use application, e.g., floor and wall coverings. Analytical techniques are now available to detect volatile organic compounds (VOC) and so influence stabiliser developments to improve this aspect.

Barium Cadmium (Ba Cd)

Ba Cd-based systems (which may also include zinc) have been available for many years due to their excellent cost effectiveness in combination with good initial colour and long-term stability. However, in the European area, their use was voluntarily phased out by the PVC industry in 2001, due to severe restrictions relating to environmental and toxicity (carcinogenic) concerns over cadmium (which accumulates in the body). Ba Zn stabilisers were the preferred option.

Cadmium-based stabilisers are still used in the USA and Asia Pacific areas, but are coming under increasing health and environmental scrutiny. Ba Zn systems have been and continue to be developed.

Barium Zinc (Ba Zn)

Ba Zn-based systems now have the majority market share for stabilisation of PVC-P in Europe due to extensive formulation development based on increasing the barium content and the important role of organic co-stabilisers. Examples of organic co-stabilisers are the diketone dibenzoylmethane, dehydroacetic acid and pyrrolidine-2,4-diones.

Calcium Zinc (Ca Zn)

Traditionally Ca Zn has been less effective as a heat stabiliser, but much work has been carried out to develop more sophisticated and higher efficiency heat stabilisers, primarily to replace Ba Zn. This is based on the fact that barium is a heavy metal. However, there is no evidence of health or environmental concerns. Barium does not build up in the body and in the USA, the Environmental Protection Agency has concluded that barium is unlikely to cause cancer in humans by ingestion. It is also not regulated in air.

Components of Ca Zn stabiliser systems are similar to those present in Ba Zn but vary in concentration.

In Europe, the annual production figure of European Stabiliser Producers Association (ESPA) members for liquid Ba Zn and Ca Zn is approximately 14 kt (*www.vinyl2010.org*).

3.2 Plasticisers

Plasticisers are added to PVC to achieve flexibility and workability. The flexibility or softness is determined by the type of plasticiser and level used in relation to the PVC (phr). They also operate as an internal lubricant between the PVC molecules. Based on high-boiling organic esters, e.g., phthalates, adipates, trimellitates, phosphates, and so on, addition levels can be as low as 20 phr for semi-rigid to 100 phr for very flexible applications.

Plasticisers act to reduce the glass transition temperature (T_g) of PVC. For many uses a reduction of T_g to ambient temperature is required. When PVC is heated in the presence of a plasticiser, the plasticiser penetrates and swells the resin particles. This results in the polar groups in the PVC resin being freed from each other and plasticiser polar groups interacting with the resin polar groups. As long as there is sufficient compatibility between polymer and plasticiser, the plasticiser will be retained in the flexible product that results. There is no chemical reaction between the plasticiser and the PVC and so it can be considered as a two-phase blend. The action of these materials is known as external plasticisation.

The ability of PVC to accept high plasticiser levels is attributed to regions of order (microcrystallites) within a predominantly amorphous polymer structure, being reduced but not eliminated by incorporation of the plasticiser. Plasticisers are held in solution by dipolar attraction within the amorphous regions whilst inter-chain association, through the microcrystallites, provides elastic recovery from deformation.

The internal structure of fully processed PVC-P is far from homogeneous. In addition to inhomogeneity at the molecular level, there is evidence for retention of some particulate structure even when, for practical purposes, it is regarded as being fully fused.

3.2.1 PVC/Plasticiser Compatibility [3, 4]

Any theoretical treatment of plasticiser/polymer compatibility is likely to refer to the solubility parameter (σ). Compatibility occurs when there is a close match of values between the plasticiser and polymer repeat unit. Various calculations for solubility parameters are available, namely Hildebrand (using cohesive energy density) and Hansen (extending this approach to include dispersion, polar, and hydrogen-bonding components in a three-dimensional space). It has been shown that solubility parameters are capable of classifying plasticisers of a given family in terms of their compatibility with PVC, but are of limited use for comparing different family groups.

The polarity parameter (Φ) has also been developed for predicting the relative compatibility of ester plasticisers with PVC. Van Veersen and Meulenberg proposed the A_p/P_o polarity ratio, which shows a good correlation with plasticiser activity. This ratio is equal to the number of carbon atoms present in the plasticiser molecule (excluding aromatic and carboxylic acid carbon atoms), A_p, divided by the number of ester (polar) groups present, P_o. This is then correlated with the molar mass of the plasticiser. Low values indicate high compatibility and give useful prediction of monomeric plasticiser activity. However, results show that the polarity ratio alone is not able to compare plasticiser activities from different families.

Neither parameter seems to apply to polymeric plasticiser compatibility.

A rapid practical test for ranking the compatibility of different plasticisers with PVC is the solution temperature or solid–gel transition temperature (T_m). This is the temperature at which a heterogeneous

mixture of excess plasticiser and a controlled reference suspension-PVC resin is observed to change to a single phase. Low solution temperature is indicative of high compatibility and good processability.

Interaction and activity parameters have also been used to measure compatibility. The Flory–Huggins interaction parameter (χ) utilises a statistical mechanical treatment of a lattice model of polymer solutions. This was applied to plasticisers by Anagnostopoulos to calculate the interaction parameter on the basis of the solid–gel transition temperature and using the molar volume of the plasticiser. Results show a good indication of ease of processing for a given plasticiser with a given resin, but will not give estimates of plasticising performance in the final product.

It should also be borne in mind that plasticiser compatibility limits can be influenced by the presence of other plasticisers and organic additives, particularly if they have a lower compatibility [5].

3.2.2 Plasticisation Process

Two stages occur during the plasticisation of PVC. The first stage is gelation, whereby the PVC particles adsorb the plasticiser due to an increase in temperature. This results in a weak gel. The second stage is fusion, resulting from further heating (above 150 °C), whereby the PVC particles and the plasticiser melt together giving a homogeneous material. Six steps have been identified that occur during these stages [6] after mixing:

- Plasticiser molecules irreversibly penetrate the porous PVC structure.

- Plasticiser adsorption occurs with plasticiser solvating the resin surface.

- Plasticiser absorption occurs with PVC particles swelling and the total volume of the material decreasing. The temperature depends on the plasticiser solvating capability.

- As the result of applied heat, major changes occur with the plasticiser forming clusters among the polymer segments, penetrating into the molecular structure. The mixture becomes a melted homogeneous material.

- With continued application of heat, the material behaves like a fluid melt.

- With cooling, the polymer hardens due to crystallisation and the creation of weak van der Waals forces and hydrogen bonding between the plasticiser molecules and the polymer segments. These changes may take hours or days (to develop the mechanical properties to a maximum).

Various theories have been developed to explain the mechanism of plasticiser action in PVC. Classic theories are based on lubricity and gel formation. The free volume theory followed on some years later.

3.2.2.1 Lubricity and Gel Theories

The lubricity theory, attributed primarily to Kirkpatrick, Clark, and Houwink [7-9], is based on the assumption that the resin rigidity arises from intermolecular friction which binds the chains together in a rigid network. When heated, these frictional forces are weakened, allowing the plasticiser molecules between the chains. Some solvent action is also suggested. Once incorporated into the polymer bulk, the plasticiser molecules shield the chains from each other, so preventing the reformation of the rigid network. However, this theory cannot explain why some materials are efficient plasticisers while others are not.

The gel theory [10] extends the lubricity theory by suggesting that the plasticiser acts by breaking the resin–resin attachments and interactions, and by masking these centres of attachment from each other, so preventing their reformation. The polymer structure is maintained by an internal three-dimensional honeycomb structure or gel.

An empirical approach [11] has analysed the prerequisites for a polymer to be plasticised. For PVC, the polymer chains are sufficiently long to have some strength even though the plasticiser forces them apart. In addition, PVC chains are linear and the crystallinity is very low, with chlorine atoms separating chains to reduce van der Waals forces and forming dipoles that act as points of attraction between nearby chains. If a liquid is introduced into the PVC polymer with the same order of cohesion energy as the polymer, it will remain stable. Polar groups in a plasticiser are essential for good compatibility. When plasticiser molecules are introduced into the polymer mass, polymer chains are separated by the smaller liquid molecules, which are then able to line up their dipoles with the polymer dipoles.

3.2.2.2 Free Volume Theory

The free volume theory extends the lubricity and gel theories and also allows a quantitative assessment of the plasticisation process.

Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. The free volume is derived from the specific volume and it has been established that the specific volume of polymers decreases linearly with the temperature until the T_g is reached [12]. Unplasticised PVC is seen to possess very little free volume, whereas resins, which are flexible in their own right, are seen as having relatively large amounts of free volume. Plasticisers act to increase the free volume of the resin and also to ensure that the free volume is maintained as the resin–plasticiser mixture is cooled from the melt. By combining all three theories, it can be seen that plasticiser molecules not interacting with the polymer chain must simply fill free volume created by those molecules that do. These molecules may also be seen to provide a screening effect preventing interactions between the neighbouring polymer chains, thus preventing the rigid polymer network reforming on cooling.

In PVC-P, free volume can arise from motion of the main chain, side chains, and chain ends. These motions can be increased by increasing the number of end groups, increasing side chain length, including segments of low steric hindrance and low intermolecular attraction, and so on.

3.2.3 Plasticiser Influence on Physical Properties

The primary criterion for assessing a plasticiser's effect on the properties of PVC is softness or hardness (see Section 4.3.1). Shore A hardness is the most commonly used international scale. British Standard softness is a scale running in the reverse direction. As plasticiser levels increase, the hardness, of course, decreases and the elongation at break increases. Tensile strength and 100% extension modulus decrease.

The flexibility of plasticised PVC is strongly temperature dependent with reversible stiffening and embrittlement at low temperatures (see Section 4.3.3, **Figure 4.5**). The low-temperature performance of plasticisers is assessed by cold flex temperature (the temperature at which the torsional modulus of rigidity of a PVC-P sheet reaches a standard value) and cold crack temperature (the temperature at which 50% of a set of specimens are fractured by a standard impact) (see Section 4.4.6, **Figure 4.6**).

Electrical insulation properties such as volume resistivity (see Section 4.5.1) are dependent on plasticiser structure.

The incorporation of any plasticiser detracts from PVC's flame retardancy. This applies even to the superior flame retardant properties obtained from addition of phosphate or chlorinated paraffin plasticisers.

3.2.4 Plasticiser Choice and Selection [13]

The main factors that influence plasticiser choice are determined by the specification requirement of the finished product and depend on:

- Manufactured cost including formulation and processing (how easily the formulation can be processed and formed into the end product). Plastisol viscosity, if appropriate, would also come into this category.

- Compatibility – to ensure the flexible material remains stable and free of component separation during service.

- Plasticisation efficiency – the correct plasticiser type and the level of addition necessary to achieve the required modification of PVC end properties.

- Permanence including migration resistance, extractability, and volatility under service conditions.

3.2.4.1 Migration Resistance/Extractability

Since the liquids used as PVC plasticisers are completely miscible with other organic liquids, contact between PVC-P and oils or solvents results in plasticiser depletion. The fastest extraction of plasticisers is shown by low molecular weight polar solvents, such as esters, ketones, and ethers. With such extractants, absorption by the PVC is an important factor, since it opens up the polymer structure thereby facilitating plasticiser migration.

For applications involving prolonged contact with oils, fats, greases, or solvents, acceptably low rates of extraction can be achieved by the use of polymeric plasticisers (see Section 3.2.5.11). For complete extraction resistance, the use of a plasticising polymer (see Section 7.3.1) would be necessary.

Another aspect to consider is if the PVC-P is in contact with another polymer for which the plasticiser has some affinity. Plasticiser migration can occur across the polymer interface resulting in softening and blistering of surface coatings, adhesive bond failure, and environmental stress cracking of rigid thermoplastics. The effects are greatest for plasticisers with linear structures, low molecular weight, and a solubility parameter matching that of the receiving polymer.

3.2.4.2 Migration/Volatility

Since plasticisers are not bound chemically to the polymer and are held by relatively weak intermolecular forces, most are capable of migrating to the surface. From there an evaporation process may be possible into the surrounding atmosphere, depending on the temperature. It is this migration aspect that has resulted in so much of the discussion around environmental and health

issues (see Section 9.2.3.1). In addition, transmission into the atmosphere at ambient temperature of the plasticiser residues, within an enclosed space, has also raised concerns regarding indoor air quality influencing the health of occupants.

The large-tonnage phthalate plasticisers, used in most PVC-P applications, have molecular weights in the range 390–450. While their vapour pressures at ambient temperature are too low to measure, with increasing temperature the rate of evaporation increases rapidly to a point where plasticiser depletion can have a serious effect on physical properties. Hence volatility is one of the primary performance criteria for plasticisers and defines their suitability for service at elevated temperatures. Volatile loss of plasticisers from PVC-P in service is nearly always controlled by evaporation rate, diffusion through the polymer being sufficiently rapid to replenish surface loss.

The cable industry uses a spectrum of plasticisers with different levels of volatility according to the rated temperature of operation of the end product.

The automotive industry is also concerned with the volatility of plasticisers used in car interior trim. Windscreen fogging is the reduction of clarity of the windscreen caused primarily by condensation of plasticiser vapour.

At PVC processing temperatures, the rate of volatile loss of plasticisers is orders of magnitude higher than in end-product service. Plasticiser process fumes are eliminated by incineration or scrubbing of the extracted exhaust air prior to emission into the atmosphere. In some applications, it is desirable or necessary to select plasticisers to minimise fume generation.

3.2.4.3 Stability in Service

At service temperatures in excess of 70 °C, atmospheric oxidation of plasticisers can lead to changes in mechanical properties exceeding the effects of plasticiser depletion caused by volatile loss. Decomposition of peroxy groups present at low concentrations in the oxidised plasticiser leads to initiation of dehydrochlorination of the PVC polymer. The effect is generally most marked for plasticiser structures containing branched alkyl groups, such as diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). It is common practice for a hindered phenolic antioxidant, diphenylol propane, to be incorporated at a level of 0.1–0.5% in plasticisers used for high-temperature applications.

Plasticiser selection has a strong influence on the photostability of PVC and this plays a part in formulation for applications to be used outdoors. The first step in natural photodegradation is absorption of solar ultraviolet (UV) radiation. This effect is shown, to varying degrees, by aromatic esters but not by aliphatic esters. The subsequent formation of damaging free radicals is then favoured by the presence of branched alkyl chains. Thus, adipates show better UV stability than straight chain phthalates, which in turn are better than branched chain phthalates.

The weak link in the structure of most plasticisers is the ester group which can be broken at ambient temperatures by both alkaline hydrolysis and by esterases (enzymes present in widely encountered micro-organisms). Both mechanisms are influenced by steric factors, the most linear ester structures tending to show the greatest susceptibility to breakdown. The use of microbiocides is covered in Section 3.9.

3.2.5 Plasticiser Types

Plasticisers are often classified according to their particular functions. These can be as follows:

- Primary – which means that it has a sufficient level of compatibility with PVC to be able to be used as sole plasticiser at all addition levels giving a useful modifying effect.

- Secondary – has limited compatibility with PVC and normally can only be used in mixtures with a primary plasticiser.

- Extender – can be used as a lower cost, partial replacement for a primary plasticiser.

- General purpose/commodity – can be used as a primary plasticiser in almost all PVC-P applications giving satisfactory performance at optimum cost.

- High temperature – low volatility and resistant to loss during service at relatively high air temperatures.

- Low temperature – resistant to reversible stiffening and embrittlement of PVC-P at low service temperatures.

- Non- or low-migratory – exhibits a low level, or rate, of migration into materials with which the plasticised product comes into contact in service (can be air, liquids, and solids). This will be very dependent on the nature of the extracting medium.

- Fast fusing – may also be called highly solvating and indicating strong intermolecular interaction with the polymer, together with rapid penetration. Permits the use of lower processing temperatures and/or shorter process times.

- Low viscosity – gives low viscosity and good viscosity stability to PVC plastisols at relatively low plasticiser levels. Normally has low viscosity itself.

Table 3.2 gives a feel for the large range of plasticisers available to the formulator to meet performance requirements linked to satisfactory processability.

3.2.5.1 Branched and Linear Phthalate Esters

The most common plasticisers are the family of phthalate esters produced by the esterification of phthalic anhydride with various branched or linear alcohols (**Figure 3.2**). R can be C_6 to C_{13} with C_8, C_9, and C_{10} esters being the most common.

(R = Alcohol chain)   **Figure 3.2** Phthalate esters

Table 3.2 Plasticiser types and applications		
Plasticiser type	Characteristics	Typical use
Commodity phthalate esters		
C_8	Good fusion rate and viscosity (plastisols).	General purpose and reference point for comparison. Medical devices.
Di-2-ethylhexyl phthalate (DEHP)/dioctyl phthalate		
Diisooctyl phthalate		
C_9	Slightly less efficient but lower volatility than C_8. Move to this category from C_8 for health and environmental issues.	
DINP		Toys and general purpose.
C_{10}		
DIDP		General purpose with good low-temperature performance.
Di-2-propylheptyl phthalate		Cable.
C_7	Good solvation.	
Diisoheptyl phthalate		Flooring/coating plastisols.
C_{13}	High gelation temperature. Low extraction, good migration resistance.	High-temperature cable insulation.
Diisotridecyl phthalate		
Speciality phthalate esters		
$<C_8$	Fast fusing, high volatility, lower plasticising efficiency. Improved low-temperature flexibility *versus* BBP.	
Dibutyl phthalate (DBP), diisobutyl phthalate, butylbenzyl phthalate (BBP), dihexyl phthalate		Flooring.
C_{11} Diisoundecyl phthalate	Low-volatility isophthalate.	
C_7–C_{11} L911P, L810P, L711P, L9P, L11P	Linear and semi-linear phthalates for low-volatility and low-viscosity applications.	Low temperature, low fogging.
Trimellitate esters		
Tris-2-ethylhexyl trimellitate (TEHTM)/trioctyl trimellitate (TOTM)	Better extraction and migration resistance. Good high-temperature but poorer low-temperature performance.	High-specification electrical cable insulation and sheathing. Medical devices.
Trimellitate ester of mixed semi-linear C_7 and C_9 alcohols (L79TM)		Automotive interior (low fogging).
Trimellitate ester of mixed C_8 and C_{10} linear alcohols (L810TM)		
Aliphatic esters		
C_8	Improved low-temperature performance, higher volatility. Low-viscosity plastisols.	Blending plasticiser. Used in combination with polymeric plasticiser for food cling wrap.
Di-2-ethylhexyl adipate (DEHA)/dioctyl adipate (DOA)		

Table 3.2 Continued		
C_9	Much less volatile than DEHA.	Phthalate blends.
Diisononyl adipate (DINA)		
C_{10}		
Diisodecyl adipate (DIDA)		
C_8	Superior low-temperature performance, good flexibility, inferior extraction resistance.	Specialised applications with extremely demanding low-temperature flexibility (cable sheathing).
Di-2-ethylhexyl sebacate (DOS), di-2-ethylhexyl azelate		
C_{10}		
Diisodecyl sebacate (DIDS)		
Phosphate esters		
Isobutylated or isopropylated triaryl phosphate esters. Alkyl aryl phosphate esters. Trialkyl phosphate esters	Flame retardants with excellent permanence.	Electrical cable and general applications requiring flame retardancy – tents, conveyor belting, and so on.
Secondary plasticisers		
Chlorinated paraffins	Have some compatibility constraints and can influence heat stability.	Used in conjunction with primary plasticisers to give volume cost savings.
Chlorine content (52%)	Similar volatility to C_8 phthalate.	Flooring, cable, extrusion, and sheet.
Chlorine content (45%)	Low viscosity, good low temperature.	Plastisols (flooring, wall covering), moulding, and hose extrusion.
ESBO, epoxidised linseed oil, octyl epoxy stearate or tallate	Primary use as secondary heat stabilisers but also impart flexibility. Compatible only at relatively low addition levels.	General use.
Polymeric plasticisers		
Polymeric adipates of differing molecular weight. Phthalic polyesters. Caprolactone-derived polyesters	More difficult to process/less compatible but excellent resistance to extraction. High cost.	Applications requiring excellent permanence and chemical resistance.

3.2.5.2 Branched Phthalates

2-Ethylhexanol, the feedstock for DEHP, is derived from propylene. Isononanol and isodecanol, used to manufacture DINP and DIDP, respectively, can be produced via the so-called 'oxo' route, based on polygas olefins, by the carbonylation of the olefin. This process (hydroformylation) acts to add a carbon atom to the olefin chain by reaction with carbon monoxide and hydrogen under temperature, pressure, and catalyst conditions. Polygas olefins are mixtures with carbon numbers between 6 and 12, synthesised from C_3/C_4 refinery olefin streams. Due to the distribution of the C=C double bonds in the olefin and the varying effectiveness of certain catalysts, the position of the

added carbon atom can vary and an isomer distribution is generally created in such a reaction. The precise nature of this distribution can vary. Consequently, these alcohols are termed isoalcohols and the subsequent phthalates isophthalates. DINP and DIDP, manufactured this way, are C_9 rich and C_{10}, rich, respectively. An alternative isononanol process for DINP is based on a C_8 olefin produced by dimerisation of *n*-butene. This type has a less branched structure and while interchangeable with the polygas-derived DINP, some performance improvements can be observed.

DEHP, DINP, and DIDP are subject to EU risk assessments (see Section 9.2.3.1).

3.2.5.3 Linear Phthalates

The alcohols used for linear phthalates are generally mixtures produced by hydroformylation of linear α-olefin fractions derived from ethylene. In practice, these alcohols contain between 50 and 80% straight chain components, the remainder being lightly branched.

The main linear phthalate used in Europe is based on C_9–C_{11} alcohol mixtures (designated 911P or L911P or di (nonyl, undecyl) phthalate).

In the USA a wider range of linear phthalates are available, due to pricing being closer to the commodity branched chain phthalates. Therefore, the L711P product, based on a 70% linear C_7/C_9/C_{11} alcohol, has been established for some time.

In addition, mainly linear phthalates based on C_9 (dinonyl phthalate) and C_{11} (diundecyl phthalate) are available. A mean chain length of 11 is the practical upper limit for linear phthalate plasticisers, due to increased melting points for phthalates with higher chain length.

3.2.5.4 Links between Structure and Performance of Phthalate Plasticisers

The dependence of phthalate properties and performance on alkyl carbon number and degree of branching is well known and follows the following general rules.

Increasing the carbon number gives:

- Lower density, higher viscosity, and, for linear phthalates, higher melting point.

- Lower volatility, slower migration, lower extraction by polar media.

- Slower PVC processing requiring higher temperatures to compensate.

- Reduced softening efficiency at normal temperature, but improved cold flex properties.

Reduced branching gives:

- Lower viscosity.

- Tendency to freeze to give waxy solids, rather than progressively increasing in viscosity as temperature is lowered.

- Reduced volatility, but faster migration.

- Slightly lowered compatibility with PVC in the presence of secondary plasticisers.

- Slightly improved softening efficiency at normal temperatures and significantly better cold flex properties.

- Better thermooxidative stability and photostability.

- Reduced resistance to chemical hydrolysis and biodegradation.

3.2.5.5 Butylbenzyl Phthalate (BBP)

This is by far the most important product in the benzyl phthalates category and is produced by the reaction between the sodium salt of monobutyl phthalate and benzyl chloride (**Figure 3.3**).

Figure 3.3 Butylbenzyl phthalate

Due to its chemical asymmetry, it is a highly solvating plasticiser for PVC and is the reference standard for fast fusion. Its major use is in cushion vinyl flooring and sealing compounds. BBP is subject to EU risk assessment (see Section 9.2.3.1).

3.2.5.6 Phthalate Alternatives

Several alternatives to phthalate esters have been promoted, primarily due to the considerable media, legislative, and scientific attention given to phthalates. Most suggested alternatives already have a niche use in specific PVC-P applications, but have still to undergo extensive data generation for risk assessments.

Alkyl sulfonic phenyl esters (Mesamoll, Lanxess Deutschland GmbH) have been proposed to replace DEHP/DINP in toys, coated fabrics, sheet, film, and so on. They have very good processing characteristics with high hydrolysis resistance in performance.

Benzoate esters have already been used for some time, particularly in the USA. Dipropylene glycol dibenzoate is a highly solvating plasticiser used as an alternative to BBP in flooring. New blends have been introduced for plastisols also to replace DINP. The replacement of DBP is also possible.

Di-isononyl-cyclohexane-1,2-dicarboxylate (Hexamoll, DINCH, BASF AG) has been developed for so-called sensitive markets, covering toys, medical devices and food contact applications. Advantageous toxicological profiles, in comparison to some phthalates have been identified.

Citrate-based esters, particularly acetyl tri-*n*-butyl citrate, although much more expensive, have extensive specialist use in medical and food packaging films (US Food and Drug Administration, BgVV/BfR (German Federal Institute for Risk Assessment) approval). They have also been proposed as an alternative to DINP for toys, and so on, and to DEHP for medical devices. Additional esters are tri-*n*-butyl citrate, acetyl tri-*n*-hexyl citrate, and *n*-butyryl tri-*n*-hexyl citrate. Citrates are generally perceived as being low-risk products from the health, safety, and environmental viewpoints.

3.2.5.7 Trimellitate Esters

Trimellitates are produced by esterification of alcohols (ranging from C_7 to C_{10}) with trimellitic anhydride (TMA). TMA is similar in structure to phthalate anhydride with the exception of a third functionality on the aromatic ring (**Figure 3.4**). Consequently, esters are produced in the ratio of three moles of alcohol to one mole of anhydride.
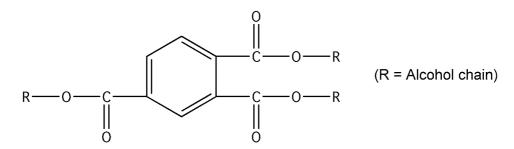

(R = Alcohol chain)

Figure 3.4 Trimellitate esters

Their higher molecular weight and bulkier molecular structure (relative to general purpose phthalates) give them lower volatility and generally greater extraction and migration resistance. Consequently, they are used in high-specification electrical cable and sheathing, and in automotive interior applications where windscreen fogging is important.

TEHTM (TOTM) is the most competitively priced and most widely used trimellitate. It is one of the very few plasticisers also accepted for use in medical devices, where its low migration favours its use in preference to DEHP. Examples are haemodialysis tubing and blood platelet storage containers.

L810TM has a particularly good combination of high- and low-temperature performance. Triisononyl trimellitate is also well established in the USA.

3.2.5.8 Aliphatic Esters

These esters of aliphatic dibasic acids have a similar structure to adipates, as shown in **Figure 3.5**.

Azelates are based on $(CH_2)_7$ and sebacates are based on $(CH_2)_8$. Both are based on natural product-derived acids (sebacic acid from castor oil), resulting in high and variable prices relative to adipates.

(R = Alcohol chain)

Figure 3.5 Aliphatic esters

Adipates are the most important plasticiser in this category with alcohols of similar chain length (C_8–C_{10} range) to those used in phthalate manufacture being esterified with adipic acid.

Adipates show some similar activity to phthalates but are more expensive. They have the benefit of very low viscosity and therefore are relevant for plastisols. Low-temperature flexibility is also good. However, they have higher volatility and higher migration rates. As a result, adipates are used in blends with phthalates to produce a compromise of properties.

DEHA (DOA) is the adipate used in greatest tonnage, particularly in PVC clingfilm in combination with non-migratory polyester plasticisers. DEHA is approved for food contact use within particular addition levels.

DINA and DIDA have limited compatibility in PVC and are primarily used as blending plasticisers.

The most important sebacate plasticiser is DOS which has the best low-temperature performance of any commercial plasticiser. It is also much less volatile (as expected) than DEHA. DIDS is also used. Sebacate and azelate esters have lower plasticising efficiency.

3.2.5.9 Phosphate Esters

Phosphate plasticisers have the structure shown in **Figure 3.6**.

where R_1, R_2 and R_3 are alkyl and/or aryl groups

Figure 3.6 Phosphate esters

The great majority of production is of triaryl phosphates, particularly isopropylated. These are followed by the alkyl/aryl type in which R_1 and R_2 are alkyl groups and R_3 is phenyl.

The principal advantage of phosphate esters is their improved flame retardancy relative to phthalates. This is due to the formation of thermally stable pyro or polyphosphoric compounds after pyrolysis which forms a protective vitreous barrier.

The phosphates of isopropyl phenols/phenol mixtures are highly solvating plasticisers for PVC and confer more resistance to ignition and combustion than other phosphate esters.

The alkyl/aryl phosphate 2-ethylhexyldiphenyl phosphate has widespread use in flexible PVC applications. This is due to its combination of properties of plasticising efficiency, low-temperature performance, migration resistance, and fire retardancy.

The trialkyl phosphate, tris-(2-ethylhexyl) phosphate is recommended for good low-temperature resistance linked to good weathering and fire retardancy.

3.2.5.10 Secondary Plasticisers

Chlorinated paraffin plasticisers are produced by the controlled chlorination of straight chain paraffin fractions. The general formula is $C_nH_{2n+1}Cl$ where n is typically 14 to 17. These are called medium chain chlorinated paraffins (MCCP). Chlorine contents can range from 30 to 70%, but for PVC the most relevant grades contain 45 or 52% chlorine. Chlorinated paraffins have extensive use in other industries, such as metalworking and cutting fluids.

Chloroparaffins have insufficient compatibility for use as the sole plasticiser in most applications. Their use as secondary plasticisers is fairly extensive as they are significantly cheaper. They also have much greater resistance to ignition and combustion than general purpose plasticisers. Consequently, they can also be used to partially replace phosphate ester plasticisers. In some applications, an adverse effect on the thermal stability of PVC is a constraint on their use.

The use of MCCP in Europe is currently under investigation in accordance with the Existing Substance Regulations (EEC No. 793/93) (see Section 9.2.3.3).

Epoxy compounds used as PVC additives have a dual function. Firstly, their epoxy group content causes them to function as auxiliary heat stabilisers, enhancing the effectiveness of mixed metal-type stabilisers. Secondly, they have the type of structure that makes them effective plasticisers. They have limited compatibility with PVC and typical addition levels are <8 phr.

Epoxy stabilising plasticisers are of two types called epoxy oils and epoxy esters. Epoxy oils have high molecular weight and bulky structures which provide resistance to migration. Epoxidised soya bean oil (ESBO) is the most important in this group and is manufactured by epoxidation using hydrogen peroxide of refined soya bean oil. It has food contact approval (within certain limits) from various regulatory authorities. Oxirane oxygen content (epoxy level) is in the region of 6.5%.

Epoxy esters are derived from synthetic alcohols and natural product unsaturated acids. Octyl epoxy stearate (from oleic acid) is the most common product in this category. It has lower molecular weight and more linear structure than ESBO, which confers low viscosity and good low-temperature properties. Oxirane oxygen content is in the region of 4.5%, which theoretically means it is less effective than ESBO as a heat stabiliser but this is difficult to observe in practice.

3.2.5.11 Polymeric Plasticisers or Polyesters

Polyester plasticisers are typically saturated polycondensates of glycols with dibasic acids, most are typically based on propan-1,2-diol or butan-1,3-diol and adipic acid. Differing molecular weights are available to suit particular needs.

Polyester structures may be chain terminated by the inclusion of a monobasic acid or monohydric alcohol (2-ethylhexanol). Non-terminated polyesters contain acidic or hydroxy end groups which are beneficial in enhancing resistance to extraction by hydrocarbons. However, other performance aspects may be reduced.

An alternative form of polyester structure can be obtained by ring-opening and self-condensation of a lactone and some commercial polyesters are based on caprolactone with neopentyl glycol. These are low-melting-point paste solids that show processing advantages over more conventional polyesters.

For applications requiring good extraction resistance and heat ageing, polymeric esters are used. They are normally described as non-migratory plasticisers due to their resistance to extraction by hydrocarbon oils, vegetable oils, and solvents and their reduced migration into polymers (particularly non-polar types). A major application is for food contact approved use in PVC clingfilm.

Other applications exploiting the migration resistance of polyesters are high-temperature electrical tape, coated fabrics, solvent-resistant cable hose and tubing, and pond and tank liners.

These materials are relatively expensive. In addition, their lower compatibility and high viscosity (of some grades) makes them more difficult to handle and process.

3.3 Impact Modifiers

Unmodified PVC-U has relatively poor impact strength at, and below, ambient temperatures and the inclusion of an impact modifier significantly improves its performance, in particular the notch sensitivity (sensitive to stress concentrations at the notch).

Impact modification is achieved by incorporating rubber domains into the polymer matrix, which, of course, must fit well within the matrix. Good dispersion and adhesion to the PVC matrix is essential.

The mechanism for impact improvement depends on the rubber component being able to absorb impact energy without the propagation of crazes and cracks.

Examples of the different generic types of impact modifier that can be added to PVC formulations are:

- Methacrylate–butadiene–styrene (MBS) terpolymer

- Acrylate–polymethacrylate copolymer (acrylic)

- Chlorinated polyethylene (CPE)

- Ethylene–vinyl acetate copolymer (EVA)

- Acrylonitrile–butadiene–styrene terpolymer (ABS)

Addition levels are typically 5–12 phr and the incorporation of impact modifiers can influence gelation and melt viscosity. Having limited compatibility with PVC, it is believed that the impact improvement is achieved via the interruption of the homogeneous morphology into a heterogeneous structure.

Acrylic modifiers have good processing characteristics linked to reduced die swell and good outdoor weathering stability. Their use in window profile and siding applications is well documented. Based on a crosslinked butylacrylate elastomer core and polymethacrylate shell technology, produced by emulsion polymerisation, the elastic core of the modifier has a hard shell to keep the product free flowing and couple the modifier to the PVC matrix. Much work has been carried out covering various aspects of their processing and performance characteristics. Important criteria are:

- Influence on weld strength in window frame manufacture.

- The relationship with gelation level on impact strength and morphology.

- The effect on impact strength of varying crosslinking levels in the rubber component of the impact modifier.

- Relationships between melt flow and mechanical properties.

New and updated acrylic impact modifier grades are regularly being developed to meet demands for higher output with a broader processing window.

CPE impact modifiers contain around 35% chlorine and are thermoplastic in nature. With a similar melting point to PVC, they initially form a network structure which changes to a particulate structure on processing. They also have good processability and excellent weathering performance - consequently they are also used for window profiles. CPE also acts as an internal lubricant providing improved flow characteristics to the PVC polymer melt. The incorporation of relatively small amounts has been shown to improve the strength and toughness of PVC pipes.

MBS impact modifiers also depend on core shell technology, with a polybutadiene/styrene core and a polymethyl methacrylate/styrene shell. They have a wide use in PVC applications, particularly for clear packaging (bottles, film, and sheet), as the refractive indices of PVC and the modifier are similar. They are also used in pipes and fittings. They are particularly efficient for low-temperature impact improvement but are not suitable for outdoor applications.

EVA copolymers mixed with PVC are also available for impact modification with good weathering resistance. They also generally confer a lubricating action requiring modification to the lubricating system of the formulation.

Specific ABS terpolymer modifiers also process well in clear applications giving low crease whitening and excellent chemical resistance. The heat distortion temperature of ABS-modified compounds can be higher in comparison to MBS-modified componds. They are not suitable for outdoor applications.

Impact performance can be measured by different techniques (see Section 4.3.4):

- Falling weight impact – consists of a dart-shaped mass, of a specific weight, falling from a standard height onto the extruded material. The temperature at which this test is carried out is usually −10 °C. The results depend on formulation, gelation level, and profile shape.

- Tensile impact – this is a high-speed tensile test using a pendulum weight. This test is linked to the intrinsic material formulation.

- Notched impact – pendulum weight impacter. ISO 180 [14], ASTM D 256 (Izod) [15], and ISO 179-1 (single V-notch Charpy and double V-notch Charpy) [16].

It is also important to recognise the way a specimen breaks. Ductile fracture (hinge break) shows stretching or elongation until failure. There is also whitening around the broken area. Brittle fracture (complete break) occurs with little deformation happening during failure. The difference can be due to temperature, where brittle fracture occurs at lower temperatures. Alternatively, brittle fracture can also occur if insufficient impact modifier has been used or dispersion is poor.

3.4 Process Aids

Process aids are added primarily to PVC-U (including foam) to improve fusion characteristics and melt flow during the processing stage. They can also be added to improve the processability of semi-rigid PVC formulations. Addition levels are typically from 1 to 6 phr with resultant improvements in output and surface finish. Transparency can also be improved in clear formulations. Chemically, these products are either acrylic polymers (methyl methacrylate or acrylate) or styrenic copolymers (containing methacrylate). The molecular weight and T_g control their efficiency. Having high compatibility with PVC, these high-molecular-weight materials entangle the shorter PVC chains and transfer the shear generated during processing to promote fusion. The effects of processing aids can be summarised as follows:

- Melt homogeneity improvement by promoting the breakdown of PVC particles and ensuring that a homogeneous melt is obtained. Good melt homogeneity is essential for achieving good physical properties and surface finish.

- Melt strength improvement as a result of their compatibility. Good melt strength is essential for blow moulding, high-speed take off from calenders or extrusion lines, and foam applications.

- Melt extensibility and elasticity improvements to permit wider operating conditions and higher outputs.

Processing aids with a lubricating effect are made through variation of the chemical composition to give a less compatible material. This results in little effect on PVC gelation but helps metal release and reduces plate-out.

3.5 Lubricants

Lubricants classically function in two ways: (1) externally to reduce friction between the polymer melt and hot metal surfaces during processing; and (2) internally to reduce frictional forces within the polymer matrix and, in so doing, lower the effective viscosity. External lubricants, by definition, have poor compatibility with PVC and migrate to the surface to create metal release. Internal lubricants are more compatible, have high polarity, and are therefore more soluble in PVC. Both types are essential for processing of PVC-U formulations, particularly taking account of the differing shear conditions resulting from extrusion, calendering, or injection moulding. In practice, most lubricants have both external and internal characteristics, but vary in the ratio of one to the other in the way they perform. However, the correct balance and type of internal to external and addition level are crucial due to the influence on gelation level, plate-out of incompatible materials in the die and calibration equipment, and physical properties.

The main chemical classes that make up lubricants are all waxes or soaps and are as follows:

- Amide wax – ethylene bisstearamide (EBS) has a balance of internal and external behaviour.

- Hydrocarbons, which can be split up as:

    - Paraffin waxes – linear alkanes with chain lengths varying from C_{20} to C_{50} which are very external in nature. The lower molecular weights show some internal character.

    - Polyethylenes (PE) with molecular weights ranging from 500 to 1000 (C_{35}–C_{70}) with linear or branched molecular chains, differing from the paraffin waxes in end groups.

    - Oxidised polyethylene waxes which result from oxidation of PE waxes causing breaks in the molecular chains and the formation of acid groups. They are very external in nature because of excellent metal release characteristics.

- Esters of many types such as:

    - Glycerol esters such as the liquid glycerol monooleate (GMO) and the solid glycerol monostearate (GMS) which are mostly internal functioning with GMS having some external properties.

    - Montan esters, obtained from brown coal, and consisting of montanic acid esters with long chain aliphatic alcohols. Chain length is in the region C_{28}–C_{34} with a broad range of lubricant functionality and high compatibility. Particular use is in profile and calendered formulations.

- Fatty acids such as stearic acid (can be a mixture of C_{16} and C_{18}) or hydroxy stearic acid. External lubricating behaviour with some internal lubrication.

- Metallic soaps, in particular calcium stearate, which acts as an internal lubricant by improving flow but increases internal shear and mould release. Also acts as an acid scavenger. It is a very commonly used lubricant.

Assessment of lubrication performance, on a processing machine, is carried out taking account of energy consumption (motor load, screw speed, and output), surface finish, melt flow, and physical properties. In the laboratory, gelation measurement based on time and melt viscosity is carried out using a torque rheometer or mill. This takes account of the internal lubrication effect (lowering of melt viscosity with no significant change on fusion or mill stick times) and external lubrication (little influence on melt viscosity but does significantly influence fusion or mill stick times).

The addition level of internal lubricants can be in the region 0.3–1.0 phr, whereas external lubricants are added at much lower levels, e.g., 0.05–0.3 phr.

For extrusion and injection moulding of PVC-U formulations, it has become common practice to use one-packs, comprising of the stabiliser and a balanced lubrication package, which are formulated to match the particular processing and end-use performance requirements.

In PVC-P applications, the plasticiser acts as an internal lubricant and external lubricants can be added to increase output, and so on. Excessive levels or incorrect choice can cause problems with post-treatment, e.g., printing or blooming on ageing.

3.6 Fillers

For most PVC-U and PVC-P applications, fillers are added primarily to reduce formulation cost, but some are also used to enhance properties and performance. There is a balance between the cost

benefits and any acceptable deterioration in physical properties that could result. The density of the final product will increase, of course, at higher filler levels.

Another important aspect is the influence on processing with respect to output, plate-out, and surface finish.

3.6.1 Calcium Carbonate

Calcium carbonate (also known as chalk) is the most commonly used filler for PVC. This material is mined as calcite mineral, milled, and classified to a particular particle size range. Surface treatment with stearic acid can be carried out with the stearic acid converting to calcium stearate in the process. This results in improved processing and dispersion (mechanical properties) and improved moisture resistance giving better electrical properties.

Synthetically precipitated calcium carbonates (PCC) are manufactured from the natural material by calcination, hydration, recarbonation, and precipitation from solution to give a fine particle size suitable for use in high-performance areas. Surface treatment is also normal.

Particle size is important and, for some applications requiring good weathering and impact performance (window profiles), the ultrafine milled, high whiteness, natural version is normally used. Coated ultrafine and precipitated calcium carbonates are also claimed to have a positive effect on impact properties in impact-modified formulations. The abrasive wear of calcium carbonate on melt processing equipment is not considered significant but increases with increasing levels.

Chalk fillers also have extensive use in PVC-P applications where the particle size restriction is not so essential. Higher addition levels can also be accommodated. They are extensively used in wire and cable where they assist, in combination with other additives, to reduce HCl generation in a fire situation. PVC plastisols generally have high filler loadings for cost reasons but need to retain the appropriate viscosity and rheology for the processing technique. Specific grades of calcium carbonate are available for these applications.

3.6.2 Other Fillers

Depending on the geographical area, ground marble fillers, some with surface treatment, are used for PVC-U and PVC-P applications.

Ground dolomite (calcium magnesium carbonate) and limestone fillers are also used.

Talc has been used in calendered PVC compounds to increase melt cohesion and modulus of the finished material.

Calcined kaolin clays can be used in footwear (improved abrasion resistance) and cable (improved insulation properties). Kaolin has a use in plastisol formulations giving good rheological control.

3.7 Flame Retardants (FR) and Smoke Suppressants (SS)

PVC-U formulations have low flammability due to their chlorine content. This is because the chlorinated radicals react with highly reactive radicals (HO$^\bullet$ and H$^\bullet$) to give less reactive radicals which decrease the kinetics of the combustion.

The addition of plasticiser in PVC-P formulations necessitates the use of FR and SS additives for those applications where flame retardancy is required. These additives are known as functional fillers and a correct balance is necessary to achieve all the end-use specification requirements. They are predominately used in cable, conveyer belting, and roofing membrane formulations to give resistance to fire initiation and propagation. It is also important to reduce dripping in a fire situation and that as little smoke (including acid fumes) as possible is generated.

Antimony trioxide (Sb_2O_3) has been used extensively, usually in combination with phosphate ester plasticisers, giving excellent fire performance without too much influence on mechanical properties. The FR mechanism is activated by the formation of volatile antimony trichloride ($SbCl_3$) and antimony oxychloride (SbOCl) which act as radical scavengers and flame poisons. However, antimony trioxide is a suspected carcinogen and work is ongoing to replace or reduce the levels used. In addition, increased smoke evolution is seen to be a negative aspect of the use of this material.

The most recent work has involved reducing smoke emissions, a previous weakness of fire retardant PVC-P formulations. Aluminium trihydrate and magnesium hydroxide have been shown to create low smoke levels and much reduced toxic gas emission. The activity of these materials is a function of the vaporisation of their water of hydration.

Zinc borate is also an effective SS (particularly in combination with phosphate ester plasticisers) and may replace antimony trioxide. In addition to the Lewis acid effect of $ZnCl_3$ in promoting crosslinking and char formation, zinc borate may act as a low-melting glass which together with mineral hydrates and metal oxides can provide a protective barrier to impede burning.

The combination of ammonium octamolybdate and zinc stannate is also beneficial from the flame retardancy and smoke suppression aspects.

The use of a mineral based on magnesium/calcium carbonate/hydroxide has also been promoted.

It should be noted that the use of functional fillers can cause a dramatic deterioration in physical properties and processability at the addition levels necessary to achieve the requirements of flame retardancy and smoke suppression.

The use of impact modifiers and process aids in PVC-U construction products will detract from flame retardancy. Under upcoming EC standards, based on a standardised flame test method, new Euroclasses (2000/147/EC) for reaction to fire for construction products, possibly including smoke performance, will be introduced (see Section 4.6.6). This may require the incorporation of low levels of FR and SS.

3.8 Pigments

Pigments for PVC must be thermally and light stable, have good dispersability, and be compatible within the formulation. They may also need to satisfy specific regulations covering the end use, e.g., food contact, toys, and so on. Inorganic pigments are the most common type.

3.8.1 Titanium Dioxide (TiO$_2$)

Titanium dioxide pigments are used to give 'bright' whiteness and opacity. They play a very significant part in PVC pigmentation.

The opacity of a pigmented material is a function of its surface reflectivity, the refractive index of the pigment relative to the binder system, and its light scattering power. The light scattering capability is a function of particle size and/or absorption of incident light. Rutile TiO_2 has a refractive index of 2.76 in relation to PVC at 1.54, indicating the reason for its use. TiO_2 can have two crystal structures, rutile and anastase. Rutile is used in plastic applications, due to higher refractive index, better light scattering efficiency, and superior UV absorption.

Production for plastics grades is normally via the chloride process where the chloride is generated prior to conversion to the oxide.

Commercial grades are based on multilayer inorganic materials over a TiO_2 core. The layers can be silica (SiO_2) and/or alumina (Al_2O_3) which act as a barrier between the core and the resin to minimise photocatalytic degradation of the polymer. Interaction between UV radiation, moisture, and an uncoated TiO_2 surface produces free radicals, which can then oxidise the resin binder by photocatalytic degradation. There may also be a surface treatment to improve dispersion and compatibility. A controlled particle size distribution is also necessary.

Grades are available with different undertones such as a blue clean white, more neutral, and cream. These characteristics can be expressed on the brightness L* and tone b* colour scales (see Section 4.7.3).

Another term used in relation to TiO_2 pigments is durability. This relates to the weathering performance and light stability. Poor durability can mean loss of surface gloss, chalking (physical loss of pigment, as the surface is degraded), colour change, and, in the extreme, mechanical breakdown.

As explained above, in the presence of oxygen and moisture, some of the UV energy absorbed will be converted to chemical energy in the form of reactive chemical radicals. These slowly attack the polymer at the exposed surface. This weathering process is observed when tiny pits form around the embedded pigment particles. Specific TiO_2 non-chalking grades are used in PVC-U applications in Europe and significantly contribute to outdoor weathering performance by delaying this process. Addition levels are in the region of 4.0 phr.

Lower cost, controlled chalking grades of TiO_2 may be used in some PVC-U tin-stabilised applications (siding, fencing, and so on) in the USA. Addition level is significantly higher at around 10 phr. These grades operate by developing a level of chalking to maintain the specific whiteness and cleanliness of the surface over the weathering period.

Titanium dioxides for use in PVC plastisols must satisfy the need for good wettability and dispersion within a liquid medium. Paste storage stability (flocculation resistance) is also important. Aluminosilicates as pigment extenders to replace partially TiO_2 in plastisols are also available.

3.8.2 Other Inorganic Pigments

Lead (sulfo) chromate and lead chromate pigments give yellow coloration. Iron oxide is also used for yellow pigmentation. Lead (sulfo) chromate/molybdate gives an orange effect. Ultramarine blue (a sulfur-containing sodium aluminium silicate) is also used for toning or shading purposes.

Lead chromate pigments, traditionally used for pipe and cable applications, are linked with the phase-out of lead-based stabilisers. Special pigment systems based on organic or organic/inorganic combinations are available.

3.8.3 Organic Pigments

Organic pigments have high tinting strength combined with shade brilliance. They cover almost the entire colour spectrum. They are normally used in combination with inorganic pigments, particularly TiO_2, which give the opacity. Carbon black pigment may also be added at low levels as a shading component.

Typical chemical types are:

- Copper phthalocyanine (blue and green)

- Diazo condensation products (yellow, red, and brown)

- Diazo compounds, such as diarylides (yellow)

- Polycyclic compounds, such as dioxazine (violet), quinacridone (red and violet), and isoindolinone (yellow)

- Monoazo compounds, such as benzimidazolone (orange) and the azo salts (yellow)

Pigments are classified by a standardised colour index (CI) system, covering chemical type, application, hue, and physical forms. Hue indication is further classified into shade fields. The Society of Dyers and Colourists has developed and maintains this system (*www.sdc.org.uk*).

3.8.4 Pigment Concentrates and Masterbatches

The earliest type of pigment masterbatch took the form of dispersion in a plasticiser, which resulted in a paste for adding to PVC-P formulations.

More recent developments in pigmenting technology relate to ease of handling, low dust or dust free, colour concentrates, and masterbatches for PVC-U and PVC-P applications. Some are also suitable for dosing on line. Such technology covers dispersion in waxes, encapsulation (microbeads), and use of polymer-based carriers, including PVC. Concentrates and masterbatches can be supplied in a fully colour matched formulation.

3.9 Microbiocides

PVC-P materials, such as flooring and roofing material, can be prone to microbiological attack in humid or damp conditions. This can be due to micro-organisms, such as algae, bacteria, and fungi, using the plasticiser at the surface of the article as a nutrient carbon food source. This can lead to partial discoloration (pink colour or black specks) which can further cause a tacky surface where dirt can accumulate. Unpleasant odours may also be a consequence.

Biocides function by becoming active on the surface of the material to destroy micro-organisms. Constant microbiocide transfer to the surface is necessary at a rate sufficient to maintain an effective concentration at the surface. This is achieved by the process of diffusion of the plasticiser within the material, the organism also acting as a leaching solvent. Addition levels of the active ingredient are at the 400–2000 ppm level and the active biocide is normally supplied dispersed in a plasticiser or ESBO carrier.

Based on their thermal stability, compatibility, permanence, and broad-spectrum performance against different fungi, the most common microbiocides are 10,10′-oxybisphenoxyarsine (OBPA), 2-*n*-octylisothiazolin-3-one (OIT), and 4,5-dichloro-2-*n*-octylisothiazolin-3-one (DCOIT).

Various laboratory and accelerated outdoor test methods are available to determine the effectiveness of microbiocides in simulated performance situations covering weathering, water leaching, and resistance to soil burial. These are the areas where performance can be negatively influenced.

Some of the microbiocides mentioned previously also have some limited bacteriocidal activity but specific antibacterial additives may also be necessary to provide protection against bacterial infestation.

In Europe, the Biocidal Products Directive (BPD; 98/8/EC) could influence future use of particular microbiocides. The legislation aims to establish a positive list of biocide-active substances and a national authorisation of biocidal products containing active substances on the positive list. Each product must have a dossier that contains information on its biocidal efficacy, physical, chemical, and analytical properties, toxicological and ecotoxicological properties, environmental effects, and, where appropriate, any effects if brought into contact with food. The aim is to establish that the biocide is sufficiently efficacious without having unacceptable effects.

3.10 Blowing Agents

Blowing agents are solid materials that decompose to release gases at particular temperatures matching the appropriate melt viscosity necessary to retain a foam structure. There are two main types: (1) azodicarbonamide ($H_2NCON=NCONH_2$), which is exothermic in nature and decomposes at ~215 °C to give primarily nitrogen gas, but also NH_3, CO, and CO_2, and (2) sodium bicarbonate ($NaHCO_3$), which is endothermic and so absorbs heat as it releases carbon dioxide gas over a wide temperature range, which coincides with the processing temperature window of PVC-U foam. Various grades are available to suit particular applications and both have well-controlled particle size distribution.

The azo compounds, particularly suitable for PVC-P formulations for flooring, wall covering, leather cloth, and so on, must be specially formulated to include an activation agent, which catalyses the earlier decomposition, and so increases the total gas evolved at a lower temperature to suit the melt viscosity. Occupational exposure to azodicarbonamide dust should be avoided and granular forms improve handling. Plasticiser damped versions are also available. The foam formation depends on the gelation rate and the rheological characteristics of the gelled/fused plastisol, the rate of gas formation during the gelation phase, and the rate of heat transfer during the foaming of the plastisol. Food contact approval (sealing gaskets) for azodicarbonamide (ACDM) is being withdrawn by the EC. This is based on the presence (below 25 parts per billion – ppb) of semicarbazide, a decomposition product, of unclear toxicity. Essentially, this was based on the detection capability of new analytical techniques.

PVC-U foams incorporate sodium bicarbonate as the blowing agent (see Section 6.4.2.4) giving a fairly coarse cell structure in inward foaming formulations. ACDM is used in the PVC-U free foaming process, giving a fine cell structure, but a very thin surface skin.

The mechanical foaming of PVC-P pastes has been carried out for some time on the basis of air or gas being whisked into specially formulated plastisols, which are cured using microwave or infrared ovens. The lightweight material is used for sound deadening, gasket compounds, and domestic applications such as carpet backing.

3.11 Antioxidants and Light Stabilisers

Primary antioxidants, such as hindered phenols, operate as effective radical scavengers to protect the PVC material during processing and in use (preventing photodegradation). They react with peroxy radicals via hydrogen donation to prevent hydrogen abstraction from the polymer backbone. Phosphites and esters of 3,3-thiodipropionic acid are also used as secondary antioxidants to extend the efficiency of the primary antioxidant by reduction of oxidation intermediates. These can be added at very low levels at the polymerisation stage and in combination with the stabilising package.

Light stabilisers also prevent photodegradation. UV absorbers, such as hydroxybenzophenone or hydroxyphenyl triazole types, operate by absorbing and dissipating UV radiation as thermal energy prior to potential degradation of the polymer. No permanent chemical change occurs, so activity is retained. Addition levels and sufficient polymer thickness are critical to ensure enough absorption takes place to retard effectively photodegradation.

Hindered amine light stabilisers (HALS) are also used. They are based on derivatives of 2,2,6,6-tetramethylpiperidine and act to inhibit polymer degradation by slowing down the photochemically initiated degradation reactions. Significant stabilisation is achieved at relatively low addition levels. A cyclic process operates whereby the HALS are regenerated during the stabilisation process.

Essentially, UV radiation, temperature, and moisture can initiate material degradation (see Section 4.11.2).

3.12 Other PVC-P Additives

3.12.1 Antistatic Agents

Antistatic agents are added to PVC formulations to prevent the build-up of static electrical charges, which could lead to an electric shock or a spark causing a fire in a dusty or flammable area. Dust build-up is also reduced.

By adding an antistatic agent (complex non-ionic or cationic materials) at 5–12 phr, the surface resistivity is reduced, along with a reduction in static charge accumulation. These agents function by the formation of an antistatic layer on the surface, which by attraction of moisture and in combination with the antistatic agent itself conducts away charges.

The addition of antistatic agents can have a detrimental effect on processing, particularly heat stability, and this aspect needs to be taken into account.

An alternative method of achieving antistatic performance, although not so permanent, is to apply a coating after fabrication.

3.12.2 Viscosity and Rheology Modifiers

PVC plastisols or pastes should have a viscosity and rheology suitable for the manufacturing process, in addition to handling and storage requirements. Paste PVC resins (or blends of resins) are designed to satisfy a particular rheology profile, but sometimes the addition of a viscosity depressant is necessary. This would result in a lower and more uniform viscosity to allow easier processing, permit higher filler

levels, and eliminate the use of volatile solvents for controlling viscosity. Chemically, the products are similar to those used as antistatic agents with addition levels in the range 2.0–4.0 phr.

Rheology control additives can be added to give shear thinning rheology behaviour. At low shear rates, it is essential that the plastisol be highly viscous to prevent settlement during storage, sag after application, or penetration of a textile substrate. During application, at higher shear rates, viscosity should be as low as possible for easy application and to give good flow and levelling for a smooth even film. This behaviour may be obtained by a combination of different PVC resins with different rheological behaviours to achieve the desired rheology profile. Fumed silicas are typically used to give an overall thickening effect which leads to good anti-sag and anti-settling performance. Calcium sulfonate gels are also available for this purpose with the advantage of not influencing the viscosity at high shear.

3.12.3 Bonding Agents/Adhesion Promoters

PVC plastisols spread onto industrial fabrics based on polyester or polyamide fibres require the addition of a chemical bonding agent to improve the interfacial adhesion. Based on aromatic polyisocyanurates dispersed in a plasticiser they function by reacting with the polar groups in the synthetic fibre to give strong chemical bonding at the interface of the fabric and PVC. These materials are highly compatible with the plastisol but also reactive and the plastisol formulation has to take this into account in relation to plastisol viscosity build-up on standing. Typical areas of use are truck tarpaulins, air-supported coated fabric structures, and protective clothing. Typical addition levels are 3–5% of the total plastisol formulation.

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4 Testing and Properties

The mechanical and thermal properties of polyvinylchloride (PVC) are dependent on:

- The K value (molecular weight) of the PVC resin used.

- The various formulation additives appropriate to the end-use application.

For the purposes of this book, the comparison will be restricted to unplasticised-PVC (PVC-U), impact-modified PVC-U, plasticised-PVC (PVC-P), chlorinated PVC (PVC-C), and PVC-U foam (where applicable).

Information for this chapter has been obtained primarily from the Rapra Plastics Design Guide [1], MatWeb, the materials information source (*www.matweb.com*), and Hydro Polymers (*www2. hydro.com/HPS*).

4.1 Density

The typical density of PVC-U materials is 1350–1420 kg/m^3, which is higher than other thermoplastics, due to the chlorine content. Polyethylene (PE), polypropylene (PP), polystyrene (PS), and acrylonitrile–butadiene–styrene (ABS) have densities in the region of 900–1050 kg/m^3. The density is relatively unaffected by the molecular weight of the resin. Polyethylene terephthalate (PET) has a similar density to PVC.

PVC-P can have a density range of 1350–1700 kg/m^3, this wider range due to the influence of plasticiser content and other additives (particularly fillers).

PVC-C has a higher density, 1470–1520 kg/m^3, due to the higher chlorine content.

PVC-U foam density can vary, but is in the region of 700 kg/m^3.

4.2 Water Absorption

On the basis of ASTM D570 [2], water absorption for unmodified PVC-U is 0.1%. For impact-modified rigid and plasticised PVC, the water absorption can be 0.1–0.4%. This is somewhat higher than that of polyolefins and PET (0.01–0.02%).

4.3 Mechanical Properties

Mechanical properties are inevitably important properties, because most end uses involve mechanical loading under a particular service conditions. PVC, like other thermoplastics, is a viscoelastic material and mechanical properties depend on time, temperature, and stress. The influence of operating environment generally must be considered. Typical mechanical properties are shown in **Table 4.1**.

Table 4.1 Mechanical properties						
Property	Unit	PVC-U	Impact-modified PVC	PVC-P	PVC-U foam	PVC-C
Hardness, Shore; ISO 868 [3]		83–84 (D)	80 (D)	60–90 (A)	40–70 (D)	
Ultimate tensile strength; DIN 53455 [4]	MPa	50–75	40–50	10–25	15	50–55
Break to elongation; DIN EN ISO 178 [5]	%	10–50	30–100	150–400	10–15	23–50
Flexural strength; DIN EN ISO 178 [5], DIN EN ISO527-1 [6], DIN EN ISO 257-2 [7], DIN EN ISO 604 [8]	MPa	70–90	70–80			
Modulus of elasticity (flexural modulus); DIN EN ISO 179-1 [9]	GPa	2.7	2.2–2.6		0.9–1.5	2.6
U-notch Charpy impact resistance; DIN 53453 [7] (20 °C)	kJ/m^2	2–5	5–20	No break		
Double V-notch Charpy impact resistance; (23 °C)	kJ/m^2		40–75			

4.3.1 Hardness

Hardness is defined as the resistance of a material to deformation, in particular permanent deformation, indentation, or scratching. It is a relative term and should not be confused with wear and abrasion resistance.

The hardness test is used for measuring the relative hardness of soft materials and is based on the penetration of a specific indentor forced into the material under specified conditions. Two types of durometer are used, differing in the shape and dimension of the indentor. No units are attributed to hardness numbers. Shore A hardness is used for relatively soft materials and Shore D hardness for harder materials. The plasticiser content and type influence Shore A hardness (see **Figure 4.1**).

The Rockwell hardness test (ISO 2039-2; [10]) may also be quoted for rigid PVC formulations. This measures the net increase in depth impression as the load on an indentor is increased from a fixed minor load to a major load and then returned to a minor load. Hardness numbers (without units), in increasing order of hardness, are R, M, and E scales for plastics. The higher the number in each scale, the harder the material. The different Rockwell hardness scales utilise different size steel balls and different loads. Rigid PVC has a Rockwell R hardness of 80–110 depending on the grade. This can be compared with PP at 90 R, polycarbonate (PC) at 124 R, ABS at 75–115 R, PS at 100 M, and PET at 196 M.
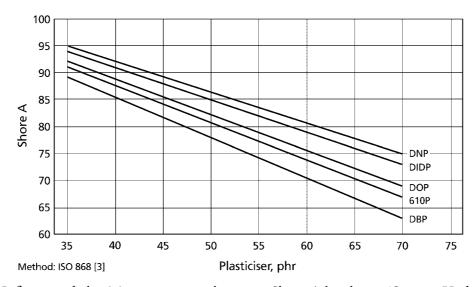
Figure 4.1 Influence of plasticiser content and type on Shore A hardness. (*Source: Hydro Polymers*) DNP: dinonyl phthalate, DIDP: diisodecyl phosphate, DOP: dioctyl phthalate, DBP: dibutyl phthalate

4.3.2 Tensile Properties

Tensile testing measures the ability of a material to withstand forces that tend to pull it apart and can determine to what extent the material stretches before breaking. Under laboratory conditions, tensile testing is carried out at a constant strain rate.

Once it has reached its high tensile strength, under a tensile load, rigid PVC flows in a plastic manner as the tensile stress is removed until plastic fracture occurs.

Tensile modulus (Young's modulus) is the force that is needed to elongate the material. For PVC-U, the tensile modulus is in the region of 3.5 GPa. The 100% modulus is the stress/strain ratio at 100% extension. In PVC-P formulations, this is influenced by plasticiser content and type (see **Figure 4.2**). **Figure 4.3** shows the relationship between 100% modulus and Shore A hardness.
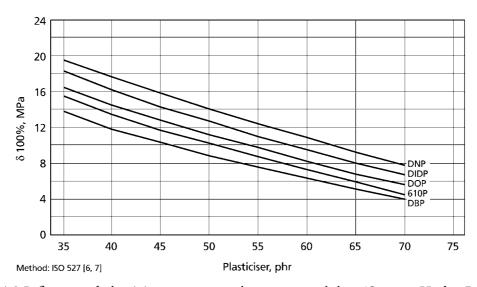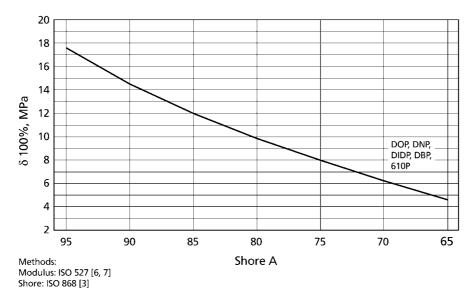
Figure 4.2 Influence of plasticiser content and type on modulus. (*Source: Hydro Polymers*)

Figure 4.3 Relationship between 100% modulus and Shore A hardness.
(*Source: Hydro Polymers*)

4.3.3 Flexural Properties

Flexural property measurement measures the stress–strain behaviour in bending mode.

Flexural strength is the ability of a material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced are a combination of compressive and tensile stresses.

Flexural modulus is a measure of the stiffness during the initial part of the bending process. **Figures 4.4 and 4.5** show the influence of temperature on flexural modulus. As expected, the influence of an impact modifier reduces flexural modulus. The superior flexural modulus at higher temperatures for PVC-C can also be seen. Increasing plasticiser content has the effect of reducing flexural modulus.
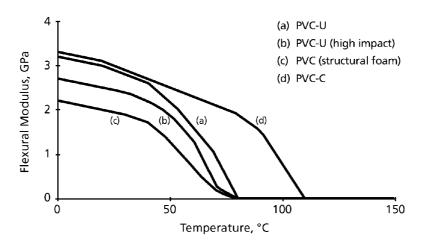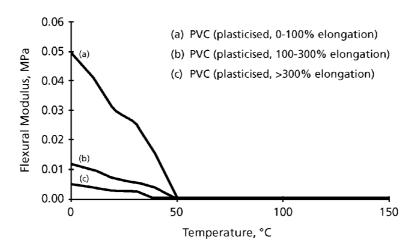
Figure 4.4 Influence of temperature on flexural modulus of various PVC-U formulations.
(*Source: Rapra Plastics Design Guide*)

Figure 4.5 Influence of temperature on flexural modulus of PVC-P formulations with differing plasticiser content. (*Source: Rapra Plastics Design Guide*)

4.3.4 Impact Properties

Impact properties are related to material toughness, with toughness defined as the ability of PVC to absorb applied energy. Impact resistance is the ability to resist breaking under shock loading or being able to resist fracture under stress applied at high speed.

The use of a pendulum impact tester is common (set up for the different striker heads and sample supports appropriate for Charpy, Izod, or tensile impact test methods) with results expressed in terms of kinetic energy consumed by the pendulum in order to break the specimen. The test result is typically the average for 5 or 10 test specimens. Charpy or Izod tests are the most common tests with impact-modified PVC (see Section 3.3).

The specimen is usually notched with the shape of the notch usually being a V-cut, but may be a U-cut. Notch depth and geometry can vary depending on the particular test method. Notching provides a stress concentration area that promotes a failure. The mode of failure should also be noted in relation to brittle (fractures without yielding) and ductile (material yields in addition to cracking). Notched impact values of unmodified rigid PVC are significantly lower due to notch sensitivity. Impact strength is still good for unmodified PVC, providing surface notches are avoided.

Notched impact testing is used extensively as an economical quality control method to assess the notch sensitivity and impact toughness. The precision of the cutting of the notch is critical and special notch cutting equipment is available to give accurate and reproducible results.

The Izod impact test (ASTM D256 [11] and ISO 180 [12]), most common in the USA, utilises a pendulum which swings on its track and strikes a notched sample, secured at one end, on the thickness where the notch has been made. The energy lost, i.e., required to break the sample, is measured from the distance the pendulum swings after impact. The result is reported in energy lost per unit of specimen thickness (J/cm) for the ASTM method or energy lost per unit cross-sectional area at the notch (J/m^2) for the ISO method, at a standard temperature (normally 23 °C). The minimum requirement for window profile, in the USA and using this test method, is 5.3 kJ/m^2 when measured under the ISO method.

The single V-notch Charpy test (BS EN ISO 179 [13], 0.1 mm notch radius) has been common in the UK and relies on a horizontally mounted sample which is supported unclamped at both ends. The pendulum hammer (of fixed kinetic energy) strikes the sample on the thickness opposite from the notched side. The crack propagates on the opposite side from the impact. The minimum accepted figure for this method is 12 kJ/m² for window profile. Brittle failure is common with this test method. ISO 179-1 [44] (0.25 mm notch radius) single notch Charpy test can also be used.

In the double V-notched Charpy test (ISO 179-1), commonly used in Germany, and results quoted in **Table 4.1**, a V-notch is cut into opposite edges of the test sample with the notches precisely across from each other. The pendulum hits the face of the horizontal specimen between the notches, with crack propagation occurring at a right angle to the impact location. A ductile behaviour results when impact tested. The requirement is a minimum of 40 kJ/m² for window profile. This test is also used to check impact retention after artificial weathering/ageing.

The new European Standard for PVC-U window profiles, EN 12608 [15], has now imposed a new Charpy test, the ISO 179-2 [16] (0.25 mm single-V notch), to quantify the impact resistance. A double-V notch Charpy test, with a notch radius of 0.25 mm, is also specified in this standard for the assessment of the impact strength retention of extruded profile after artificial weathering. The test must be performed using instrumented equipment, on samples cut from a 4 mm thick, milled and pressed plate. This plate can be prepared from either shredded profile or directly from the dry blend or compound. For impact modified material, the minimum acceptable level is 20 kJ/m². There is considerable debate that such an impact test takes no account of processing variables or profile thickness effects.

4.3.5 Fatigue

Fatigue is defined as a decline in load-bearing capacity with time under load. Under conditions of constant load, this is termed static fatigue or creep rupture.

On average, the long-term allowable stress of a plastics product, operating at ambient temperatures, is no greater than one-fifth the ultimate short-term strength of the material. As the tensile strengths of unreinforced thermoplastics mainly fall within the range 20–70 MPa, this would suggest an ambient temperature range of 4–14 MPa for allowable or safe stresses. A useful body of data exists for thermoplastic piping materials, which have been subjected to long-term pressure testing at ambient and elevated temperatures. The safe allowable static tensile (hoop) stresses for 100,000 hours (11.4 years) service are shown in **Table 4.2**.

Table 4.2 Allowable stress (MPa)				
	20 °C	40 °C	60 °C	80 °C
PVC-U	13.8	10.6	4.1	–
PVC-C	13.8	10.6	6.9	3.5
Impact-modified PVC	11.0	5.4	–	–
Medium-density PE	4.1	3.7	–	–
PP copolymer	5.5	3.1	1.6	0.6
PP homopolymer	6.9	4.1	2.2	1.2
Source: Rapra Plastics Design Guide				

Dynamic fatigue, which is the durability of plastics under cyclic loading, is generally less than under static loading, with amorphous thermoplastics, such as PVC-U, being particularly sensitive. Crack growth rates increase by a factor of 5,000 under cyclic loading with decreasing molecular weight (200,000–500,000).

4.4 Thermal Properties

Thermal properties are as important as mechanical properties, as PVC, like all thermoplastics, is very sensitive to temperature changes. The thermal properties typically determine use in low- and high-temperature applications. The mechanical, electrical, or chemical properties must be considered in relation to the temperatures at which the values are derived. Typical thermal properties are shown in **Table 4.3**.

Table 4.3 Thermal properties					
Property	Unit	PVC-U	Impact-modified PVC	PVC-P	PVC-C
Thermal conductivity	10^{-3} W/m/K	1.9	2.5	1.3–1.6	
Heat deflection temperature at 1.8 MPa; ISO 75-1, ISO 75-2, ISO 75-3 [17-19]	°C	70–82	65–82	N/A	104–115
Vicat softening point; ISO 306 [20]	°C	75–82	73–82	N/A	106–115
Linear expansion coefficient	10^6 mm/mm/K	60–80	50–100	50–200	
Specific heat capacity	kJ/kg/K	0.9–1.0	0.9–1.2	1.2–2.0	
N/A: not available					

4.4.1 Thermal Conductivity

Thermal conductivity is the rate at which a material conducts heat energy through itself. It is the quantity of heat that passes through a unit of the material in a unit of time when the temperature difference of two faces is 1 K. It obviously influences the heating and cooling of the PVC melt during processing, as PVC tends to be an insulator.

For comparison, the thermal conductivity of PP is 0.22 and that of polytetrafluoroethylene is 0.25.

4.4.2 Heat Deflection Temperature

Heat deflection temperature (HDT) is a single-point measurement and does not give any indication of long-term heat resistance. It may be used to distinguish between those materials that are able to

sustain light loads at high temperatures. The definition of HDT is the temperature at which a standard test bar deflects 0.010 in under a stated load of 1.8 MPa, as shown in **Table 4.3**. Alternatively, the load can be 0.45 MPa which would yield a different HDT. Samples are supported at each end with the load applied on top of the sample vertically and midway between the supports. The heat transfer fluid is heated at a uniform rate. The HDT of a specimen can be affected by the presence of residual stresses, causing warpage due to stress relaxation. Compression moulded specimens are relatively stress free in comparison to injection moulded specimens.

Rigid PVC has a superior HDT at 1.8 MPa to PE and PP, but is inferior to the more expensive engineering thermoplastics such as ABS, polyamide (PA) 6, PA 66, and PC.

4.4.3 Vicat Softening Point

This is also a single-point measurement with the softening point taken as the temperature at which the specimen is penetrated to a depth of 1 mm under a specified load and a uniform rate of temperature rise. The indentor is a flat-ended needle type of 1 mm^2 circular cross-sectional area.

4.4.4 Linear Expansion Coefficient

PVC, like most plastics, generally expands when heated and contracts when cooled. The coefficient of linear thermal expansion is the fractional change in length as a result of a unit change in temperature of the material. The mean coefficient is commonly referenced to room temperature.

The coefficient of linear expansion of plastics is considerably higher than metals (as used in the manufacturing process) and this difference can lead to internal stresses and stress concentrations. Mould shrinkage of PVC-U materials is 0.4%.

4.4.5 Specific Heat Capacity

Specific heat is the quantity of heat energy necessary to raise the temperature of 1 kg of a material by 1 K. In addition to the values shown in **Table 4.3**, specific heat capacity increases to 1.6–1.9 kJ/kg/K for rigid closed-cell foam.

4.4.6 Cold Flex Temperature

Cold flex temperature is covered in Section 3.2.3.

Figure 4.6 shows the relationship between cold flex temperature and plasticiser type and content.

4.5 Electrical Properties

Typical electrical properties are shown in **Table 4.4**.
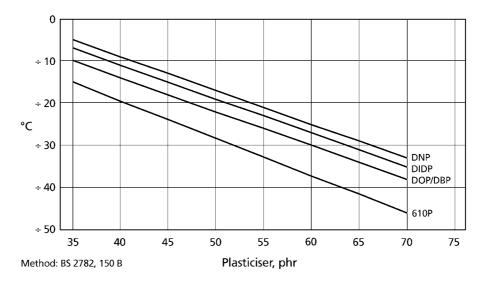
Figure 4.6 Relationship between cold flex temperature and plasticiser type and content. (*Source: Hydro Polymers*)

Table 4.4 Electrical properties				
Property	Unit	Rigid PVC	Impact-modified PVC	PVC-P
Volume resistivity (at 23 °C); ASTM D257 [21]	Ω m	$>10^{14}$	$>10^{13}$	10^9–10^{13}
Dielectric constant (at 1 MHz, 23 °C); ASTM D150 [22]		2.8–3.1	2.8–3.1	3.3–4.5
Loss modulus (at 1 MHz, 23 °C); ASTM D150	$\tan \delta \times 10^{-4}$	60–190	60–190	40–1400
Breakdown voltage (dielectric strength)	MV/m	14–20	14–20	12–16
Arc resistance; ASTM D495 [23]	s	60–80		

4.5.1 Volume Resistivity

The volume resistivity or specific insulation resistance is the electrical resistance between opposite faces of a 1 cm cube of insulating material. It is the resistance to leakage through the body of the material. High volume resistivity is desirable in applications requiring superior insulation characteristics.

Volume resistivity falls rapidly with increasing plasticiser content and this is the reason for the wide range of values shown for plasticised PVC in **Table 4.4.**

4.5.2 Dielectric Constant or Relative Permittivity

The dielectric constant is defined as the ratio of the charge stored in an insulating material placed between two metallic plates to the charge that can be stored when the insulating material is replaced

by a vacuum. Thus the dielectric constant indicates the ability of an insulator to store electrical energy. Very low dielectric constants indicate low capacitance and so have good insulation.

4.5.3 Loss Modulus or Dissipation Factor

In all electrical applications, it is desirable to keep electrical losses to a minimum. The loss modulus or dissipation factor is a measure of electrical inefficiency of an insulating material and indicates the amount of energy (heat) dissipated by the insulating material when a voltage is applied. It is expressed as the ratio of the resistive (loss) component of the current to the capacitive component of current and is equal to the tangent of the loss angle. The value is temperature dependent with higher loss modulus at higher temperature. However, PVC is not suitable for high-frequency applications due to the high loss modulus.

4.5.4 Breakdown Voltage or Dielectric Strength

The breakdown voltage is a measure of the dielectric breakdown resistance under an applied voltage. The applied voltage, just before breakdown, is divided by the specimen thickness to give the value. The result thus depends on the thickness. In comparison to other plastics, the breakdown voltage of PVC is low with reference to low-density PE (LDPE), PP, and PS. However, PVC-P formulated for wire and cable insulation and sheathing applications is used to withstand relatively high voltage without breaking down. Similarly, high electrical resistivity makes it an excellent insulator.

4.5.5 Arc Resistance

Arc resistance is the ability of a material to resist the action of a high-voltage, low-current electrical arc close to the surface. This is usually stated in terms of time required to form electrically conductive material. Failure is characterised by carbonisation of the surface (tracking or burning). Rigid PVC has a low arc resistance in comparison to other plastics, such as PE, PP, and styrene acrylonitrile.

4.6 Fire Properties

PVC-U is inherently flame resistant due to its chlorine content. When flames are in contact with rigid PVC, it forms a protective charred layer which insulates the material below and excludes the oxygen necessary for combustion. This restricts the burning zone. The hydrogen chloride emitted also acts as a combustion inhibitor. Its peak rate of heat release is low by comparison with other materials and so does not release enough heat to support its own combustion. When the flame source is removed or extinguished, PVC-U no longer burns.

The data presented in **Table 4.5** relate to typical standard formulations and not to specifically formulated flame-retarded formulations.

4.6.1 Self-ignition Temperature

Self-ignition is ignition resulting from self-heating. For comparison with the values in **Table 4.5**, wood has a self-ignition temperature of 250 °C with PE and PP at 350 °C .

Table 4.5 Fire properties					
Property	Unit	PVC-U	Impact-modified PVC	PVC-P	PVC-C
Self-ignition temperature	°C	450	450		
Flame ignition temperature	°C	390	390	315	
Limiting oxygen index; ASTM D2863 [24]	%	50	45	25–35	55–75
Heat of combustion (NBS cone calorimeter); ASTM E1354 [25]	MJ/kg	20	20–25	20–30	
Peak heat release rate (NBS cone calorimeter); ASTM E1354	kW/m^2	90–110	100–150	~200	

4.6.2 Flame Ignition Temperature

The flame ignition (or auto-ignition) temperature is the minimum temperature required to initiate or to cause self-sustained combustion independent of the heat source. For comparison with PVC, wood has a flame ignition temperature of 250 °C with PE and PP at 340 °C.

Rigid PVC is very difficult to ignite using common ignition sources.

4.6.3 Limiting Oxygen Index (LOI)

The LOI test is probably the most well-known test for flammability. The test apparatus holds a small sample which is clamped vertically in a tube, in an atmosphere where the relative concentration of oxygen and nitrogen can be changed. The aim is to test the sample flammability with a small pilot flame to find the minimum oxygen concentration required to support marginal combustion in the sample. A high LOI is indicative of a less easily ignited and less flammable material. A material with an LOI of 21% will burn freely in air (which contains 21% oxygen). For comparison with PVC, wood has an LOI of 22% and PE and PP an LOI of 17%.

4.6.4 NBS Cone Calorimeter

Heat release is a key measurement required to assess the fire development of materials and products. Oxygen depletion calorimetry is now the recognised measurement method and is based on the empirical observation that heat released by burning materials is directly proportional to the quantity of oxygen used in the combustion process. A truncated conical heater is used to irradiate a test sample at a preset heat flux in the range 10–100 kW/m^2. A typical heat flux of 50 kW/m^2 would be used for more severe fire tests for building products.

The heat of combustion of wood is slightly lower when measured with this test (17 MJ/kg) with PE and PP significantly higher at 47 MJ/kg.

The peak rate of heat release for wood is higher at approximately 300 kW/m² with PE and PP significantly higher at around 1300 kW/m².

4.6.5 Smoke Evolution

One issue concerning PVC in a burning situation is the evolution of smoke. **Figure 4.7** shows a comparison between wood, PVC, and other rubber and plastic materials based on the ASTM D4100 test method [26] (Arapahoe Smoke), cancelled in 1997. This aspect can be improved with the use of smoke suppressant additives (see Section 3.7).
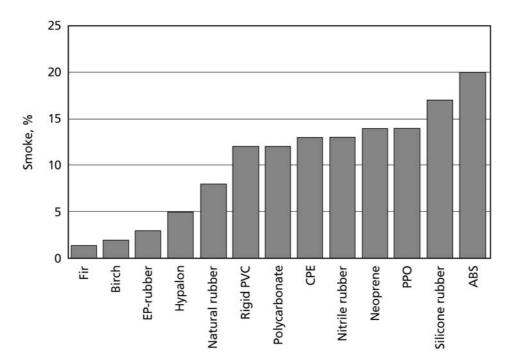
Figure 4.7 Comparison between wood, PVC, and other rubber and plastic materials based on the ASTM D4100 test method. (*Source: Hydro Polymers.*)

4.6.6 Fire Performance of PVC

Other important factors to be considered when evaluating fire performance are:

- Combustion toxicity – carbon monoxide (CO), an odourless, colourless, and narcotic gas, is produced in all fires and is universally recognised to present the greatest toxic threat in any fire situation. Low levels of this gas, which provides no warning of its presence, can cause death. PVC is no better or worse than other building materials in producing CO when burning. Other combustion products are CO_2 and HCl. Contrary to some perceptions, studies have shown that, as PVC is usually a small proportion of the mass of materials used in most buildings, HCl is produced in quantities too small to pose any unusual hazard. HCl is an irritant usually detected (painful effects on the eyes and breathing difficulties) at low concentrations and may produce the earliest effects of exposure to a fire. Studies have shown that micro-pollutants, such as dioxins, are produced in all accidental fires whether PVC is present or not [27].

- Smoke corrosion – gases produced during a typical fire can also be corrosive to metal structures and surfaces. There is no evidence that chemical reactivity from HCl gas or hydrochloric acid (when water is mixed with it) weakens steel structures [27]. However, the area of greater concern is the electronic reliability of digital equipment after a fire. Evaluations of the impact of smoke corrosivity on circuit boards have shown that PVC-P cables perform well when formulated for this application.

4.6.7 Fire Testing in the EU

There are currently a large number of different tests used across the EU for assessing fire performance. The variation and differences between the existing national tests has meant that performance comparisons of a product have been impossible. The national test methods are linked to the relevant national regulatory requirements.

The implementation of the Construction Products Directive (CPD) 89/106/EC, with its emphasis on European harmonised testing and CE marking, has resulted in extensive investigations into fire safety in the EU. In addition to reaction to fire, the CPD will also establish tests for resistance to fire and external fire spread (roofs).

The new European fire test standards will be/have been adopted directly into the national standards. Where there are conflicting existing national standards, e.g., surface spread of flame categorisation, these will be withdrawn or have their scope amended to restrict the use of products other than in construction use.

The following information is intended only to give the reader an indication of the current status on fire testing in the EU, particularly with reference to PVC products. It is not a complete overview and many issues are still under discussion.

4.6.7.1 Reaction to Fire

The Single Burning Item (SBI) Test

At the time of writing (March 2005), the SBI test method, EN 13823:2002 [28], has been introduced to harmonise across the EU, a test to determine the reaction to fire behaviour of building products (excluding floorings) when exposed to thermal attack by a single burning item. The test evaluates the potential contribution of a product to the development of a fire in a room corner near to the product. The SBI test is a room/corner test based on a propane fired sand-box burner. The specimen is mounted on a trolley that is positioned in a frame beneath an exhaust system. The reaction of the specimen to the burner is monitored instrumentally for heat and smoke release rates, and visually for physical characteristics. Fire growth rate (FIGRA) is calculated as the maximum value of the function of heat release rate *versus* time. Total heat release (THR) is also calculated. Smoke growth rate (SMOGRA) can also be determined.

This test method will be one of the methods used to categorise different performance classes for construction products, Euroclasses (2000/147/EC), for reaction to fire. Mandatory European standards are in the process of being prepared in various CEN committees to establish these Euroclasses classifications. These will eventually replace different national fire classifications. In all, seven classes, A1, A2, B, C, D, E, and F, have been established with all construction products (excluding flooring) being classified according to their performance in four tests. The F class is for performance not determined.

The SBI test is relevant for classes A2 (limited combustibility), B, C, and D (increasing fire growth and heat release rates from B through to D).

An additional classification will cover smoke release rates in one of three levels (s1 – none/little; s2 and s3 – substantial) for classes B, C, and D. E classification is assumed to generate smoke. The classification of flaming droplets/particles (d0 = none, d1, and d2) will apply to classes A2 through to D (and also E where d2 is assumed).

Radiant Panel Test for Floorings

This test, EN ISO 9239-1 [29], is designed to simulate the conditions experienced by a flooring during the early stages of a developing fire in an adjacent room. The test conditions simulate the thermal radiation levels likely to be present in this situation.

The apparatus consists of a test chamber containing the specimen mounted in a test frame on the bottom of the chamber. The radiant heat source (a porous refractory material) is heated and mounted at 30° to the horizontal at one end. A propane burner is used to ignite the test specimen, so that, when ignited, the flames generated will impinge across the specimen width. The critical heat flux at which the flame extinguishes, or alternatively after thirty minutes, is determined from the observed distances of flame spread.

A similar classification system exists for flooring products, with the classes being denoted by subscript 'fl'. This test is relevant for $A2_{fl}$, B_{fl}, C_{fl}, and D_{fl} (critical flux decreasing $A2_{fl}/B_{fl}$ through C_{fl} to D_{fl}).

Small Flame Test

The small flame ignitability test (EN ISO 11925-2 [30]) evaluates the ignitability of a product when exposed to a small flame and the test is relevant for classes B, C, D, and E and classes B_{fl}, C_{fl}, D_{fl}, and E_{fl}.

This test is the most relevant for PVC products. However, there is some concern that the good fire behaviour of PVC-U is not demonstrated in this test, particularly if smoke performance is considered. In addition, PVC, like all thermoplastics, can melt and drip leading to anomalous behaviour.

Reaction to Fire of Cables

For cables, the SBI test method is considered unsuitable for vertically mounted articles and probably the alternative test method, based on the International Electrotechnical Commission (IEC) standard IEC 60332.3 flame propagation test [31-36], will be used. This takes into account vertically mounted cable bundles, with a propane gas burner as the ignition source located at the bottom section of the vertical stack. The classification system proposal comprises seven classes, based on FIGRA - flame spread, and heat release rate, A_{ca}, $B1_{ca}$, $B2_{ca}$, C_{ca}, D_{ca}, E_{ca}, and F_{ca}, with additional classes defined for production of smoke and burning droplets/particles. There has also been a proposal from the expert working group that acidity/corrosivity should be included as an additional classification parameter for most of the classes of reaction to fire performance for cables. The viewpoint here is that the release of acidity in the case of a fire is frequently considered a risk for the safety of people and goods. Acidity is widely considered at present the best possible approach to the toxicity requirements being developed in some European countries. There is an opposing viewpoint that acidity is an inadequate parameter for assessing the actual toxicity and takes no account of the non-acidic and toxic carbon monoxide gas release. For PVC-P use in cables, the final decision and outcome could be significant.

4.6.7.2 Resistance to Fire

Fire resistance means that structural elements such as walls and flooring withstand a fully developed fire and fulfil certain requirements. All construction products will be classified according to these requirements of performance characteristics, such as load-bearing capacity (R), integrity (E), and insulation (I). Additional characteristics may apply for relevant uses and these include thermal radiation (W), self-closing capability (C), smoke leakage (S), soot fire resistance (G), and fire protection ability (K). Mechanical action (M) will also be categorised for relevant elements.

The classification periods of fire resistance are declared in minutes from 15 to 360 in particular groupings. Relevant tests are covered under EN 1363, parts 1 and 2 [37, 38] and EN 1364 [39, 40] relating to different non-load-bearing elements.

The fire testing is primarily based on the simulation of the post-flashover fire and the smouldering fire. Other tests cover constant temperature attack, external fire exposure (e.g., emerging from a window), and very hot semi-natural fire. The test selection and fire exposure conditions will vary depending on the application.

Basically, the main test involves subjecting the item to a heated furnace environment for the desired period of time. The method of measuring the heating curve now utilises a plate thermocouple to standardise furnaces across Europe. Previously, a bead thermocouple was common. This has resulted in the tested items being subjected to more heat during the early stages of the test. This may result in more difficulties in passing some classifications.

4.7 Optical Properties

The optical properties of a material can be defined in terms of refractive index, clarity or transparency/haze, gloss, and colour. The refractive index (the amount of refraction that takes place, directly connected to the speed of light in a substance) of PVC is around 1.54. For comparison, that of PP is 1.49, that of water is 1.33, and that of glass is 1.51.

4.7.1 Transparency

PVC, both rigid and flexible, has good clarity when correctly formulated. This property is utilised in many different applications.

Flexible PVC film (cling wrap) is extensivly used for packaging of food products by allowing the customer to see the product but at the same time minimising the passage of water vapour into or out of the package. It also permits naturally occurring gases to escape from the package. An industrial use, requiring excellent clarity for flexible PVC, is hanging strip doors. Rigid PVC has uses in blister packs and blow moulded bottles.

It should also be noted that clear material can also have colour. These can vary between blue clear, water clear, and neutral clear.

4.7.2 Gloss Level

Surface gloss is linked with the ability of a surface to reflect more light in some directions than in other directions. Gloss is influenced by the refractive index, the angle of incident light, and the surface topography. Glossmeters are used, whereby gloss ratings are obtained by comparing the specular reflectance from the sample to that from a highly polished black glass standard (with a refractive index of 1.567). A 60° angle (or an 85° angle for low and medium gloss) is normally used to measure gloss level. EN ISO 2813:2000 [41] is the reference standard.

Gloss level can be influenced by the formulation ingredients but is most influenced by processing equipment conditions and techniques. See also Section 6.4.2.6.

4.7.3 Colour

The final colour of a PVC article depends, obviously, on the pigments used but heat stabilisers can have an influence with colour consistency and prevention of yellowing caused by degradation. Optical brighteners, which make materials whiter and brighter under ultraviolet (UV) light, are not generally used but may have specific uses.

The technical measurement of colour is usually based on the CIE L*a*b* colour sphere or colour space to aid the numerical classification of colour differences, providing a standard scale for comparison of colour values. The light source can be varied but, of course, must be standardised for a particular colour measurement. A typical illuminant type would be D65 which relates to neutral daylight.

L* gives the level of colour intensity. For opaque materials, L* = 0 (total black) and L* = 100 (white). For clear materials, L* = 0 (total black) and L* = 100 (colourless). a* is the red to green axis with positive a* giving the degree of redness and negative a* greenness. b* is the yellow to blue axis with positive b* giving the degree of yellowness and negative b* the blueness.

Thus, a typical shade of white could be L* = 92.70 a* = +1.60 b* = −5.10 and a pale grey (nearly white) could be L* = 83.70 a* = −0.50 b* = +0.50.

Delta (Δ) values of these figures can also be generated where ΔL*, Δa*, and Δb* indicate how much a standard and sample differ from one another in L*, a*, and b*.

The total colour difference ΔE* summarises the differences of one colour in comparison with a standard, considering their L*, a*, and b* values. ΔE* does not indicate which of these parameters are out of tolerance if ΔE* is out of tolerance. The colour standard is established from the average of several readings over time.

4.8 Surface Properties

4.8.1 Abrasion Resistance

Abrasion resistance is the degree to which a surface is able to resist rubbing or wearing away by friction. The resistance to abrasion is closely related to hardness, resiliency, and the formulation. It also depends on test conditions, type of abrasive, and development and dissipation of heat during the test cycle.

Abrasion resistance is particularly relevant to flexible PVC and is influenced by the plasticiser type and level and filler content. In general, in a clear formulation, a softer material tends to abrade less than a harder one. However, in a highly filled composition, the softer material tends to abrade more. More information on the more efficient plasticisers can be found in Section 3.2.5.

A material's ability to resist abrasion is often measured by its loss in weight when abraded with an abrader. The Taber abrasion test involves placing the test specimen on a revolving turntable with an appropriate abrading wheel under a set dead weight. The weight loss after a large number of revolutions (1,000–5,000) is measured. Different (less) abrasive wheels with different loads are possible.

4.8.2 Surface Resistivity

In common with most other polymers, plasticised PVC is a poor conductor of electricity and can accumulate static charges on the surface. This can detract from the appearance of the finished article due to dust pick-up. More seriously, sparking, caused by static discharge, can occur leading to dust or solvent/air mixture ignitions.

Surface resistivity is influenced by plasticiser type and content. The polymer grade can also have an influence.

The surface resistance of a plastic is the resistance to the flow of electrical current over its surface. Results are reported in ohms and it is important to note that environmental factors, such as temperature and humidity, can greatly influence results. Low surface resistivity is necessary in applications where the dissipation of static electricity is required, e.g., conveyor belting in mining. Flexible PVC gives surface resistivity values in the range 10^{11}–10^{12} Ω.

Decreased resistivity (and so increased conductivity) is normally achieved in flexible PVC formulations by the use of additives (see Section 3.12.1). A surface resistivity of less than 3×10^8 Ω can be obtained. For example, this is the maximum surface resistivity permitted for articles used in coalmines.

4.9 Biological Behaviour

4.9.1 Assessment under Food and Water Legislation

PVC, on its own and manufactured to the current standards, is accepted as having very low toxicity (bearing in mind that no materials are truly non-toxic) and is a safe material. The maximum residual vinyl chloride monomer (VCM) concentration standard in PVC resin destined for food and medical applications is now being met at <1 g/ton. However, the main issues come with the use of different additives in the formulation and possible by-products from polymer degradation.

In addition to being suitable for the intended application, the main requirements for food contact and potable water use are that the PVC article must not impart odour or taste. Another significant criterion is the migration of additives, monomer, catalyst residues, polymer degradation products, etc., into the food or water. The migration of these species is a function of time, temperature, and extractant type. At unacceptable levels, these species could produce potential health hazards or the formation of undesirable flavours or odours.

4.9.1.1 Food Contact

The application of PVC in contact with food and water has been covered by the relevant standards/regulations by different authorities in different countries. Within the EU there have been various directives to bring together the national standards and regulations, based on the approvals already generated nationally. The most important national standards have been generated in Germany through the BfR (Federal Institute for Risk Assessment), previously BgVV and BGA, who have access on their website to databases for plastics recommendations (*www.bfr.bund.de*).

In the EU (*http://europa.eu.int/comm/food/food/chemicalsafety/foodcontact/spec_dirs_en.htm*), food contact plastics are regulated by Directive 2002/72/EC which consolidated Directive 90/128/EEC and its amendments. This directive lists approved monomers with vinyl chloride and vinyl acetate referenced in Annex II, Section A. This reference quotes compliance to a much earlier Directive 78/142/EEC that is specific to PVC.

For VCM (a known carcinogen), the EU limit states that it should not exceed 1 mg/kg (1 ppm) in the final product and that PVC articles must not transfer any residual monomer to food when tested at an analytical sensitivity of 0.01 mg/kg (10 ppb). PVC manufacturers in Europe produce PVC resin specifically for use in food contact and medical applications that meets the 1 mg/kg requirement, obviating the need for the converter to test the packaging material for residual monomer. Vinyl acetate monomer has a restriction that the migration level into food should not exceed 12 ppm.

In the USA, the Food and Drug Administration (FDA), following risk assessments carried out in different food contact applications, has taken the viewpoint that a residual VCM content of 5–50 ppb in the PVC article, depending on the application, is considered as safe.

To enforce overall and particular migration limits, special directives have set out procedures for analysis. Basic rules for migration tests, such as the conditions of contact (time, temperature, and food simulants), are supplied in Directive 82/711/EEC and amendments 93/8/EEC and 97/48/EC. If a product complies with the compositional requirements of Directive 2002/72/EC, then it can subsequently be tested for the desired condition of use. If it meets the migration requirements, then it is deemed suitable for use in applications covered by the appropriate test method. Directive 85/572/EEC gives a list of food simulants to be used in migration tests for various foodstuff types, using water, ethanol, acetic acid, and olive oil.

The Scientific Committee on Food (now the European Food Safety Authority, EFSA) evaluates the toxicological data of an additive and sets a corresponding maximum tolerable daily intake using a significant margin of safety. The directives (90/128/EEC consolidated into 2002/72/EC) have now established:

- An overall migration limit of 10 mg/dm² of material per article or 60 mg of substance/kg of foodstuff or food simulants for all substances migrating from a material into foodstuffs.

- A positive list of authorised monomers and other starting substances, with restrictions on their use (such as specific migration limits, SML) were applicable. Some monomers remain provisionally authorised at national level, pending a re-evaluation by the EFSA.

- A list of authorised additives and, for some of them, restrictions on their use (such as specific migration limits). In addition there also exists national limits of authorised additives. The following deadlines have been set to transform the list of authorised additives into a positive list:

- 31 December 2006, submission to EFSA for all additives currently on national lists that have not yet been evaluated.

- 31 December 2007 at the latest, EC to establish a provisional list of additives that may continue to be used, subject to national law, until evaluated by the EFSA.

- The procedures for adapting, revising, and/or completing the list of authorised substances.

Food contact plastics also include materials and articles that are in contact with water intended for human consumption, but do not cover fixed water supply equipment.

The EU continues to work (Synoptic Document) on this 'positive list' (*http://europa.eu.int/comm/food/ fs/sfp/food_contact/synoptic_doc_en.pdf*). This document is not intended to include polymerisation aids, colorants, inks, and adhesives (although some appear). Pigment use must be selected from national lists, e.g., the French positive list of pigments or from the Council of Europe resolution on colorants. There is also discussion as to whether solvents should be included in the additive list. Substances have been split into different lists (0–9), with the aim being that those substances on lists 0–4 are included on the positive list. As an example, vinyl chloride is on list 4. Essentially, those substances on the other lists have negative or insufficient data, or have toxicity concerns. Lists W7–W9 are waiting list substances, considered as new (never having been approved at national level) and lacking requested data.

It is important to note that some of these additives can be used without restriction provided they do not exceed an overall migration limit, whereas others, such as organotin stabilisers and adipate plasticisers, have restrictions imposed on them with corresponding SML. Currently SML are based on the worst case scenario whereby it is assumed that a person may consume up to 1 kg daily of food in contact with the relevant food contact material. There are discussions concerning proposed refinements to consider a fat (consumption) reduction factor of 5 (as normal consumption is < 200 g daily in Europe) and a plastics use factor to take account of the fact that different plastics are used for packaging materials, each having a percentage share. This is similar to the Food and Drug Administration (FDA) situation, already mentioned, where the consumption factor has been derived for each plastic in relation to the types of food with which it comes into contact. The use of migration modelling is permitted, to reduce the need for complex and expensive analysis, for new product approval.

In the USA, the FDA, an agency within the Department of Health and Human Services of the federal government, has responsibility for the listing of suitable raw material ingredients, from which the material manufacturer can select for packaging materials and medical devices. The regulations also provide certain specifications regarding composition and properties. Assuming all the standards have been met, the resulting article or material is then deemed to be FDA compliant. In addition, it has also taken on board the evaluation of the impact that clearance of a packaging material may have on the environment (assessment of potential impacts from use and disposal). PVC is held up in this process at the time of writing, but PVC is still used due to earlier FDA listing under the CFR (Code of Federal Regulations) Title 21, Chapter 1, Subchapter B, particularly Part 178. The part is divided into sections identified by a chemical family and indicates physical, chemical, and compositional requirements, in addition to acceptable service conditions for food contact. There may be a maximum permitted addition level. There is usually also a limit of extractable substance when exposed to particular and relevant solvents.

Within the FDA, there is no formal process of inspection of materials produced for food contact use.

4.9.1.2 Drinking Water Approval

Drinking water safety is protected by the guidelines of the World Health Organisation (WHO).

In Europe, drinking water quality is controlled by Directive 98/83/EC. The main change, from a PVC point of view, was to reduce permitted lead content from 50 to 10 µg/l over a 15-year transition period (by 2013, with an interim standard of 25 µg/l by 2003). This was aimed at allowing time for replacing lead distribution pipes but influenced the use of lead stabilisers in PVC pressure pipe.

Another directive, known as the Construction Products Directive (89/106/CE), also includes plumbing installations. One section covers hygiene, health, and the environment, and includes pollution or poisoning of water or soil, among other considerations.

However, there is no conformity in an approval scheme, as different national approval schemes exist. As a further complication, national approval in one country may not be accepted in another member state. In the UK, government approval is required via the Committee on Products and Processes for Use in Public Water Supply (CPP) which provides expert advice with the Drinking Water Inspectorate (DWI) providing technical and administrative support to the CPP. The DWI is the technical regulator for the water companies. In Germany, the Kunststoffe und Trinkwasser (KTW) and German Association of the Gas and Water Trade (DVGW) approval processes apply. In the Netherlands, the Dutch Water Authority (KIWA) standards are relevant.

A European Acceptance Scheme (EAS) is being developed by the EC to establish a common European regulatory approach for construction products in contact with drinking water, primarily to achieve a single market for these items.

In the USA, the NSF International (formerly the National Sanitation Foundation) approval process applies via the NSF/American National Standards Institute (ANSI) Standard 61 [42]. This is recognised by the US Environmental Protection Agency (EPA) as the criteria for determining the suitability for health effects of materials that convey potable water.

4.9.2 Assessment under Medical Legislation [43]

4.9.2.1 Biocompatibility

Biocompatibility is an important concept for any polymeric material that contacts the body in the form of a medical device. It can be expressed as the ability of a material, device, or system to perform without a clinically significant host response in a specific application. The terms 'blood compatibility' and 'tissue compatibility' are often quoted and refer to blood–material or blood–device interactions, and the ability of the material to remain *in situ* without significant host response and without interfering with surrounding tissue differentiation, respectively.

PVC compounds designed for medical devices will comply with these definitions as demonstrated by an ability to pass generally recognised biocompatibility test procedures. However, in common with many polymer systems, PVC interacts with blood, biofluids, and tissue to set off a whole cascade of protein-mediated reactions, including complement activation. Some additional 25 biocompatibility parameters have been identified, some of which may assume significance in patients experiencing particular clinical complications. PVC–blood interaction studies (primarily di-2-ethylhexyl phthalate interaction) have been a major focus of ongoing research. In addition, surface modification techniques have been developed to improve the biocompatibility of PVC surfaces.

4.9.2.2 Regulatory Status

PVC compounds to be used in medical devices must meet high standards of raw material selection, process, and quality control to ensure a high degree of confidence in the finished product.

The maximum residual VCM content standard for PVC resin has already been mentioned in Section 4.9.1 and resin batches are selected specifically for use in medical and food contact applications.

In selecting polymer additives for use in medical compounds, the starting point is a food contact approval list (already covered in Section 4.9.1.1) or a chemical listing taken from a pharmacopoeia monograph.

The European Pharmacopoeia [44] is published by the European Directorate for the Quality of Medicines (EDQM). There are a number of European Pharmacopoeia monographs for polymeric materials. The specific monographs for PVC are listed in the European Pharmacopoeia 5.2:

- 3.1.10   Materials based on non-plasticised PVC for containers for non-injectable aqueous solutions.

- 3.1.11   Materials based on non-plasticised PVC for containers for dry dosage forms for oral administration.

- 3.1.1.1   Materials based on plasticised PVC for containers for human blood and blood components.

- 3.1.1.2   Materials based on plasticised PVC for tubing used in sets for the transfusion of blood and blood components.

- 3.1.14   Materials based on plasticised PVC for containers for aqueous solutions for intravenous infusion.

- 3.2.4   Empty sterile containers of plasticised PVC for human blood and blood components.

The Medical Devices Directive (93/42/EEC) and the corresponding national regulations make specific reference to the European Pharmacopoeia.

4.9.2.3 Competent Authority Approval

All EU member countries have their own competent authority to protect public health and these authorities are responsible for the implementation of the three European directives that regulate the marketing and putting into service of medical devices.

In the USA, the Centre for Devices and Radiological Health (CDRH), as part of the FDA, has responsibility for safety assessments of materials used in medical devices.

If the formulation ingredient is not pharmacopoeia listed or food contact approved, another route is to check that the finished product containing the ingredient meets US Pharmacopoeia requirements for biological testing. Alternatively, satisfactory extraction resistance testing may also indicate it can be used as a component.

4.9.2.4 Formulation Disclosure

During formal registration or licence approval, one of the requirements placed upon the medical device manufacturer is to declare details of the components used in the final medical device to the competent authorities. In the USA, the FDA operates a Drug Master File and Device Master File System which includes formula disclosures and physical and biochemical test results. This confidential file is compiled for examination by any authorised body.

4.9.2.5 Product Conformance

Manufacturing controls for PVC compound to be used in medical applications are based on established systems, such as good manufacturing practice (GMP) and quality assurance (QA) standards. In particular, formal registration to the ISO 9001 [45] scheme is now almost mandatory.

In addition to standard finished product testing specifications, PVC compounds for medical use will also include tests for ignition residue, heavy metal content, and residual VCM content.

Specialised medical testing (biological testing) is usually carried out at the final development stages only. This testing is based on major recognised standards for biological testing, primarily ISO 10993 [46], a set of harmonised standards that address the biological evaluation of medical devices. Appropriate biological tests on extracts from the compound, prepared by various extraction conditions and using appropriate media, include systemic toxicity, intracutaneous reactivity, and cytotoxicity. Appropriate biological tests, performed on the PVC compound itself, include implantation, cytotoxicity, and blood compatibility tests, such as haemolysis.

4.9.3 Sterilisation

Single- and multi-use medical devices that come into contact with humans must be pre-sterilised before use, in order to minimise the risk of infection. In the case of single-use pre-sterilised medical devices incorporating PVC materials the choice is between steam, ethylene oxide, and a radiation sterilisation process.

4.9.3.1 Steam (Autoclave) Sterilisation

Autoclaves, which use steam under pressure at a temperature of 120–130 °C for approximately 30 minutes, can be suitable for PVC materials, but they are not commonly used for this material.

4.9.3.2 Ethylene Oxide Sterilisation

Ethylene oxide (EO) gas sterilisation is widely used for single-use, pre-packed medical devices. It is very effective and can be used at temperatures below 60 °C . The sterilisation process normally takes more than four hours. EO has very good penetration ability, so the objects to be sterilised can be pre-packed in a variety of container types. PVC, in common with other polymeric biomaterials, absorbs considerable quantities of EO during the process and must be aerated for several days to ensure complete absence of the gas prior to use. However, new technology is being developed to

eliminate the need for separate aeration. PVC is generally unaffected by this treatment. However, EO is a toxic and flammable gas and its use must be controlled under proper protocols.

4.9.3.3 Radiation Sterilisation

PVC is considered to have good radiation stability (particularly in the flexible form) when formulated specifically for this application. Other polymers that have good radiation stability are ABS, PE, PC, and polyurethane. In contrast, PS has excellent radiation stability, but PP grades have relatively poor stability.

Gamma Irradiation

Gamma rays, using the radioisotope cobalt-60 source of ~1.11 x 10^7 Gbq, with a nuclear energy power output of ~5 kW, are the most widely used form of ionising radiation applied to the sterilisation of single-use medical devices. They are extremely penetrating, bringing about a lethal effect on micro-organisms without any significant temperature rise. Heat-sensitive items can therefore be sterilised in their sealed packs within the final transport container without the permeability problems associated with either EO or steam sterilisation. The dose selection is based on knowledge of the radiation resistance of various microbial species together with scientific data revealing the influence of environmental conditions on such resistance. In Europe, the choice of a minimum dose of 2.5 Mrad, which is equivalent to 25 kGy, has been widely accepted. In the USA, the dose varies according to the nature and use of the device, taking account of the numbers and sterilisation resistance of the contaminants involved. Doses are usually in the range 1.5–2.5 Mrad (15–25 kGy). This is well below the gamma radiation dose rate limit of PVC (5×10^2 Mrad) where damage, such as crosslinking and chain scission, occurs.

When PVC is irradiated (particularly after 2.5 Mrad), a yellow straw colour can develop. This is especially noticeable in formulations containing little or no plasticiser. At this stage, physical properties and biological performance are not affected, but the result is the same as the start of the PVC degradation process under heat. An equally important requirement for PVC is the prevention of further colour development (and some crosslinking) during long-term storage after radiation sterilisation. The effect can be minimised by careful selection of stabilisers and antioxidants, taking into account the need to still satisfy the various biological tests on extracts from the compound. The additives perform either as reactants, which readily combine with the radiation-generated free radicals, or as primary energy absorbers to prevent the interaction of the radiation energy with the polymer. The use of the most appropriate toning pigments can also have a positive influence.

Electron Beam Irradiation

Electron beam irradiation delivers the same results as gamma irradiation, but the source is less penetrating. It is therefore normal to irradiate individual pre-packed products under an electron beam. The electron beam, a concentrated, highly charged stream of electrons, is generated by the acceleration and conversion of electricity. The product may be treated from both sides.

A higher dose requirement than gamma irradiation is required to satisfy regulatory authorities, but the method is preferred for high-volume, low-value products. It is considered to be environmentally safer.

4.10 Resistance to Micro-organisms

Rigid PVC is not a nutrient medium for micro-organisms and is therefore not attacked by them. However, flexible PVC is a nutrient source because of the plasticiser available at the surface as a microlayer. The detrimental effects can be seen through loss of properties and change in aesthetic quality (dirt pick-up and/or odour generation). These effects are much more pronounced in warm and humid conditions. More information on microbiocides, which are added to a material to prevent the growth of micro-organisms, can be found in Section 3.9.

4.11 Performance in Service

4.11.1 Maximum Continuous Use Temperature

Maximum continuous use temperatures (**Table 4.6**) are based upon the Underwriters' Laboratories (UL) rating for long-term continuous use. It is specifically the elevated temperature that causes the ambient temperature tensile strength to fall to 50% of its unexposed initial value following exposure to that elevated temperature for 100,000 hours. The continuous use temperature is based on a sample in the absence of stresses.

Table 4.6 Maximum use temperature [47]	
Polymer	Temperature (°C)
PVC-U	50
High-impact PS	50
LDPE	50
High-density PE (HDPE)	55
ABS	70
PA 6 and PA 66	80
PP	100
PC	115

On the basis of this test, rigid PVC is at the lower end of the temperature use range, but similar to other commodity thermoplastics except PP. A maximum service temperature of 60 °C has also been quoted in various technical data sheets. PVC-C has a maximum service temperature in the region of 105 °C .

4.11.2 Stability to Light, UV Radiation, and Weathering

Degradation caused by weathering often limits the service lifetime of components made from polymeric materials. With PVC, the reasons for the deterioration in properties are usually chain scission, crosslinking, and dehydrochlorination that occur as the result of photochemical reactions involving solar UV photons and atmospheric oxygen. The chemical reactions may be accelerated by elevated temperatures caused by the warming effect of the sun. In addition, water and chemical

pollutants may accelerate these processes. Obviously, weathering is influenced by the UV intensity, i.e., geographical location.

Results of weathering can be observed in various ways: loss of gloss, chalking, and colour change. These effects are limited to the surface 'skin' and have a more cosmetic effect rather than any reduction in performance.

The role of antioxidants and light stabilisers to prevent polymer degradation in service has already been covered in Section 3.11. The role of the correct heat stabiliser package and pigment is also significant.

PVC, when suitably formulated for outdoor use, has excellent weathering properties, as the reader will be aware, with its use in many exterior applications.

4.11.2.1 Natural Weathering Testing

Different exposure sites are available across the world to test weathering performance. The choice will depend on where the product will be used. Results will also be generated quicker by exposure to harsher climates.

Florida, USA, has high levels of UV radiation, humidity, and temperature that combine to provide a subtropical environment. Arizona, USA, also has high levels of solar radiation and elevated temperatures, but with a low relative humidity, i.e., a desert climate. Different European exposure sites are also available to represent a northern European climate, an industrial environment, and a Mediterranean climate.

The most relevant point to note for any outdoor or laboratory testing is the use as reference of a formulation known to have satisfactory actual outdoor weathering.

4.11.2.2 Laboratory Weathering Testing

Because there is a need for more rapid evaluation of a material's weathering resistance than can be obtained by outdoor exposure testing, there are various accelerated light stability test methods available. Different light sources are used, with water application if required. Examples are xenon arc (gas discharge lamp, where the light source is filtered to simulate UV and visible solar radiation), fluorescent UV lamps (with specific spectral distribution and condensation devices), and carbon arc.

The prediction of photoageing stability based on accelerated laboratory testing is very difficult.

4.11.3 Chemical Resistance

PVC-U is relatively inert and is not attacked by most common and dilute acids and alkalis, petrol, oils, fats, greases, or salt solutions. It is not resistant to aromatic and chlorinated hydrocarbons, strong alkalis, and nitric acid.

Rigid PVC is widely used in chemical processing, electroplating, chemical drainage, and various water handling and distribution systems. It is generally reinforced with glass-reinforced plastic to lift operating temperatures from 60 to 90 °C and also to impart considerable physical and structural properties.

Typical resistance limits for PVC-U are:

- Sulfuric acid (80%) – up to 60 °C

- Sulfuric acid (95%) – up to 20 °C

- Nitric acid at ambient temperature

- Dry chlorine gas at ambient temperature

- Sodium hydroxide (70%) – up to 60 °C

- Sodium hypochlorite (15% average Cl) – up to 60 °C

Flexible PVC has slightly inferior chemical resistance due to the presence of the plasticiser and the effect that some materials have on the plasticiser retention within the PVC matrix. Its use as tank lining has diminished with the development of synthetic rubbers. Utilising seam welding and metal bonding techniques, PVC-P can still be used where rubber vulcanisation is impractical. Pickle tanks, containing chromic/hydrofluoric acid, are an example.

4.11.4 Permeability

All polymers are permeable to gases, vapours, and liquids to a greater or lesser extent. At the molecular level even the best-made, porosity-free plastics have intermolecular voids into which gas or vapour molecules can diffuse. As would be expected, anything that inhibits the free passage of gas or vapour will increase a material's resistance to permeation. Thus, increasing the crosslink density will decrease the permeability (see Section 7.1).

Plasticisers invariably increase the permeability because of the increased mobility of the polymer molecules and the greater free volume between the chains. Similarly, if there is a significant orientation of the polymer molecules, e.g., by blowing, stretching or calendering, the permeability is reduced.

In principle, the thickness of the material has a proportional effect on the rate of permeation, if chemical interactions between the permeant and the membrane are absent. Increasing the temperature increases the permeability. Permeation takes place in two stages: initially dissolution into the surface of the polymer, then diffusion through the material under the concentration gradient so formed.

4.11.4.1 Permeability of Water and Liquids

Water vapour permeability is an essential property when determining a material's resistance to moisture or the ability to protect contents from the transmission of water vapour.

Rigid PVC has low permeability to water and water-based products. However, plasticised PVC has a relatively high permeability and it is this factor that is used in food packaging, allowing foods such as meat and cheese to breathe. It also prevents condensation and the product can be clearly seen. Flexible PVC is also permeable to steam.

The water vapour permeability of PVC film is compared with other plastics in **Table 4.7**.

Table 4.7 Water vapour permeability of various plastics	
Polymer	Water vapour (g/mm/m^2, 24 hours)
PVC-U	1.0
PVC-P	5
Polyvinylidene chloride (PVDC)	0.1
Oriented PP film	0.1
HDPE	0.2
PP	0.3
Linear low-density PE	0.4
LDPE	0.5
PET	0.6
PC	3
PS	3
PA 6	3
Ethylene–vinyl acetate	3
ABS	3
Source: Plastics Design Guide [1]	

4.11.4.2 Permeability of Gases

PVC is valued for its vapour permeability, preventing condensation.

Rigid PVC gives very good oxygen impermeability due to its closely packed and semi-crystalline structure. Flexible PVC does not give very good barrier properties, due to the plasticiser increasing the molecular chain mobility and intermolecular distances. The relatively high CO_2 permeability of PVC-U in comparison to PET explains the use of PET for carbonated water bottles.

The permeation rate of PVC for different gases is compared with other polymers in **Table 4.8.**

Table 4.8 Permeability (mol/m/Pa/s) to gases of various plastics [48]			
Polymer	O_2 ($\times 10^{18}$)	H_2O ($\times 10^{15}$)	CO_2 ($\times 10^{18}$)
PVC-U	23	40	98
PVDC	1.3	0.7	7
PET	14	60	30
PA 6	30	135	200
PP	400	17	1000
HDPE	400	4	1000
LDPE	1100	30	5700
PC	500	470	2900
PS	580	330	4000

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5 Design

Due to the versatility of polyvinyl chloride (PVC), the potential exists for designers to create innovative designs. This can be based on the material's flexibility, clarity, aesthetic qualities, and so on. Designers have been challenged by the European Council of Vinyl Manufacturers (ECVM) to create PVC products that reflect the material's versatility and enhance people's lifestyles. To date, this has resulted in an outdoor lamp (which interacts with the surroundings), fashion wear items, and household goods (in particular seating).

An important information resource for design considerations is provided by the Vinyl Institute Inc. This is the US trade association representing the vinyl industry. The Vinyl by Design website can be found at *www.vinylbydesign.com*.

5.1 Design Considerations for PVC-U Materials

Design considerations should take account of overall long-term value (costs, reliability, and environmental impact) and end-of-life considerations (ease of disassembly and material selection for compatibility with recycling methods or disposal). In the applications discussed here, the relevance of many different local, national, and international codes and standards with which unplasticised (PVC-U) complies must be considered.

5.1.1 Pipe

A useful source of information is the *PVC Pipe Systems Manual* [1], a joint publication between WRc plc (an independent consultancy specialising in plastic pipes testing, approval, failure investigations, and development of specifications) and the British Plastics Federation's (BPF) Plastic Pipes Group (*www.plasticpipesgroup.com/pvcmanual*).

PVC-U is used in residential, commercial, and industrial pipe applications because of its resistance to corrosion, chemical constituents in water, scale build-up, and exterior pitting. PVC pipes resist bacterial build-up and maintain high flow efficiency. Having a degree of flexibility, the pipe can bend without breaking, and pipe and joint assemblies withstand pressure surges and shock. The material is resistant to impact and general wear and abrasion.

PVC pipe imparts no taste or odour to the water it transports and has no effect on water quality. Due to its low thermal conductivity, PVC pipe helps to maintain a uniform water temperature. Pipe is supplied in standard lengths, and to allow for expansion and contraction, an expansion rate of 8.5 cm for every 30 m with a 40 °C temperature change allowance must be made.

PVC-U is not used for natural gas distribution networks, with high-density polyethylene (HDPE) and medium-density polyethylene (MDPE) used almost exclusively in this area. Various reasons for

this include the high stress crack resistance, excellent fusion welding characteristics, and the fact that polyethylene (PE) can be supplied and installed in coil form.

5.1.1.1 Below Ground Drainage

Sewage pipes share many of the same design objectives as potable water pipes, but additional features are the use of generally larger diameter pipes, the presence of solids carried in the flow, the greater likelihood of exposure to contaminating materials, such as surface-active agents, usually greater burial depths and subsequently higher ground loadings, and external pressures. The majority of sewage pipes form part of a gravity flow system involving low pressures and large diameters. As a result, pipe wall stiffness is usually of greater importance than resistance to internal pressure.

The recommended maximum temperature for continuous drainage applications for PVC-U is 60 °C, but temperatures up to 90 °C can be accommodated on a short-term basis.

For foul and surface water drainage, sewage pipe is supplied in one standard colour, and in three diameters of 82–160 mm. These PVC-U pipes, being flexible, can accommodate some degree of ground movement and pressure without damage. Various standards and recommendations are available if the pipe requires protection under public highways and buildings, and so on. Push-fit joints are normally used.

High-pressure water jetting apparatus is used as a method for cleaning out accumulated solids from sewage pipe. Providing agreed pressure standards and controls are used, no damage to pipe systems occurs.

Osma UltraRib pipe is also available in three diameters, 150–300 mm, for gravity sewage systems. This has a smooth inner surface with concentric external ribs to provide good axial rigidity and enhanced radial strength without a significant increase in weight. Jointing is achieved by use of a sealing ring located over the pipe within the ribs and PVC-U moulded fittings (*www.wavin.co.uk*).

For the collection and removal of surface and sub-surface water, land drainage pipe is a single-walled, corrugated, perforated system, which is lightweight and has a high degree of flexibility for laying on a continuous basis. Various diameters are available between 60 and 200 mm. Pipe joints, bends, and so on, are based on moulded PE sections.

5.1.1.2 Potable Water Transportation

The use of PVC-U for drinking water transportation has decreased for various reasons, including early system failures in the 1970s and poor environmental image. MDPE and HDPE have become the alternative materials (based on the use for gas pipe). Although these materials are less strong and less tough, they are more ductile.

The pressure-carrying capability of a pipe is related to its wall thickness and diameter, and material strength by:

$$\sigma = P(\text{SDR} - 1)/2$$

where σ (sigma) is the design strength; P is the design pressure; and SDR is the ratio between outside diameter and wall thickness. The design strength is calculated from the long-term creep strength

(LTS) at 50 years by dividing by a safety factor: for PVC this is usually 2, while for PE it is 1.25. The difference in safety factors arises from PE being more ductile. This means that strength considerations dominate the design of PE pipes. PVC pipes are seen to be more brittle and therefore have a greater risk of not performing to their strength potential [1].

PVC-U is specially formulated for thick wall, pressure pipe applications, in one standard colour (blue in the UK) with diameters of 90–315 mm. For 1.25 MPa pressure rating, nominal wall thickness is 4.7–15.8 mm. Later developments have focused on improvements to toughness and strength, allowing reduced wall thickness with better service life.

Molecular oriented PVC (PVC-O) is available with an operating pressure of up to 1.25 MPa with sizes of 90–315 mm. Wall thickness varies from 3.0 to 7.7 mm. Higher pressure ratings of 1.6 and 2.0 MPa are also possible. PVC-O has the advantage of increased toughness (extra ductility) and lighter in weight over PVC-U, due to the reduced wall thickness.

PVC alloy formulations, which incorporate chlorinated PE, are also available for this application with good fracture toughness and impact strength properties. Wall thickness at 1.25 MPa pressure rating is 3.1–10.9 mm for pipe diameters of 90–315 mm.

All PVC pipes used for potable water are supplied with push-fit elastomeric sealing ring joints integrally formed with the pipe.

5.1.1.3 Hot Water Distribution

Chlorinated PVC can be used for hot (and cold) water distribution systems with pipe and fittings joined by solvent cement. Temperatures of 90–100 °C can be accommodated. Pressure ratings of 0.3 MPa at 90 °C are also possible. At 23 °C, the pressure rating for continuous use is 2.7 MPa.

In Europe, crosslinked PE (XLPE) and polybutylene are the favoured materials for this application.

5.1.2 Exterior Construction Applications

5.1.2.1 Windows and Doors

Specific design considerations for windows and doors need to take account of glazing requirements, hardware, thermal efficiency, security, ventilation, safety, accessibility, style and aesthetics, operating environment, cleaning, and maintenance.

In addition to the cost benefits, PVC-framed windows and doors have the added benefits of low maintenance and durability, being impervious to rot, rust, corrosion, blistering, flaking, and insect infestation.

The construction (Figure 5.1) is based on a chambered extrusion which forms the frame around the glass. Windows are manufactured using a combination of different profile shapes by fusion welding mitred corners (see Section 8.2.1.4), with vertical (mullions) and horizontal (transoms) bars either mechanically fixed or fusion welded. Most PVC-U systems for window and door construction have internal reinforcement by either an aluminium or galvanised mild steel box section. This increases profile section rigidity and in addition will limit expansion due to heat gain in hot and sunny weather.
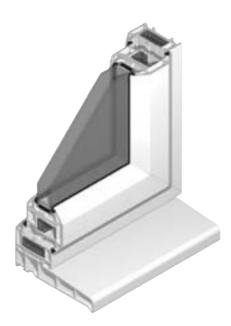
Figure 5.1 PVC-U window construction. (Source: BPF Windows Group.)

With non-reinforced PVC-U frames, movement can be up to three times more than aluminium and ten times more than wood, and this needs to be taken into account in the perimeter frame joint. (As a comparison to the value in Table 4.3, the coefficient of linear thermal expansion for aluminium is 23 and for wood it is 6.5.) Wall thickness, in Europe, is around 3.0 mm. In the USA, the wall thickness can be less. The frame extrusion depth can vary from 50 mm up to more than 70 mm with integrated drainage. Glazing can be retained by PVC-U bead of varying shapes. Gaskets and weather strips are based on ethylene propylene diene monomer (EPDM) or thermoplastic elastomer.

Sills, also based on a profile contour with end-caps, are supplied in various widths.

Handles, hinges, and so on, are located with stainless steel fixing screws with a sharp point and twin thread. Fittings can be mounted via screw channels or through the metal reinforcing section. The profile section also lends itself to multi-point locking systems.

Frame fixings for windows and doors should be between 150 and 250 mm from each corner and then at no more than 600 mm centres.

White is the most common colour but different suppliers will have their own specification shade. Other colours can be supplied in a solid form or, as a preferable and common option, by co-extrusion (see Section 6.4.2.3) or thin coat layering onto the exterior surface. Mahogany and cherry oak wood grain styles based on this technique are popular (see Section 8.1.2.2 subsection on foil coating for windows and doors).

Nearly all shapes and styles of windows and doors are possible, primarily using double glazed sealed window units. These include casement windows with tilt and turn variety, vertical sliding sash windows, sliding door and window systems, and bay windows. However, the material is not favoured widely for more traditional designs and is not acceptable for listed building use or popular in conservation areas.

The hollow chambers within the PVC profile frame provide thermal barriers that block heat transfer. In addition, PVC is not a conductor of heat or cold.

PVC window frames have been in use since the 1960s and sales have grown dramatically over the years. Life expectancy is more than 30 years. As with all windows and doors, minimum requirements for design pressure (wind load), structural test pressure (structural load), and water resistance test pressure must satisfy industry standards. The type of building, height, wind zone, exposure, terrain, and proximity to the coastline determine the window performance parameters. In addition, issues such as air permeability and forced entry need to be addressed.

5.1.2.2 Above Ground Drainage

For rainwater drainage, extruded systems are available in different colours, in half-round, semi-elliptical, and square section gutter and circular and square downpipe lengths. Sizes vary from 75 to 150 mm depending on use. Wall thickness varies from 1.5 to 3.5 mm depending on size. Joining is achieved via a clip and seal joint system, based on injection moulded PVC-U and utilising the flexible nature of this material.

Soil and waste pipe are supplied in different colours, with diameters of 82–160 mm, which can be joined by push-fit or solvent-welded joints. The solvent is usually a mixture but will contain tetrahydrofuran. The push-fit sockets, bends, branches, and so on, are also moulded from PVC-U and incorporate sealing rings. Additionally, bends, tees, and adapters can be made from acrylonitrile–butadiene–styrene for use with solvent welding, or polypropylene, including sealing rings, for push-fit sockets. Ring seals and gaskets can be made from EPDM, styrene butadiene rubber, or natural rubber.

Utilising the low-maintenance aspects of PVC-U, cladding (sidings), fascias, soffits, and bargeboards are replacing wood in these applications, in particular expanded PVC-U, which can be drilled, screwed, or nailed. Good heat insulation properties are a feature of this material with lower thermal conductivity (~0.05 W/m/K) than timber, concrete, or brick.

5.1.2.3 Exterior Cladding/Siding

Vinyl siding (solid, not expanded) is particularly popular in the USA, due to the method of building construction, and is the largest residential siding material. It cannot be used, however, on buildings higher than 15 metres. A standard panel consists of the face, a nail hem at the top where nailing slots are located, and a buttlock located on the bottom edge which locks onto the previously installed panel. The panels interlock to protect the structure of the building in addition to creating an attractive exterior finish. The extruded material is available in many colours and different embossed surface textures. It must withstand severe weather conditions. During installation, it is necessary to allow room for the siding to move in changing temperature conditions.

Products have lifetime warranties based on more than 30 years of outdoor exposure. An important consideration is to keep fire sources and easily combustible materials away from vinyl siding. However, having a relatively high flame ignition temperature (390 °C) and a much lower flame spread rate in comparison to other siding materials are to its benefit. Tests have shown that vinyl siding does not degrade the fire performance of a typical wall; in some situations, it could improve a wall's fire performance.

In Europe, the choice can also include a PVC-U hollow, chambered system with open V-jointing and expanded PVC-U systems, also with tongue and groove jointing systems. The use of a secondary waterproofing membrane, positioned against the wall and behind the supporting battens, is necessary to ensure that there is no moisture ingress into the structure. Various trim sections are also available for jointing and finishing. Cladding can be applied horizontally, vertically, or diagonally and is supplied in different colours. Fixing is at a maximum of 600 mm intervals (400 mm for coloured cladding or any cladding above two storeys high) with cladding nails. The reduced fixing location interval for coloured cladding takes into account that thermal expansion is greater, due to higher temperature build-up in darker colours. An air space of 20–25 mm should be maintained behind all cladding systems. A thermal movement of ~5 mm per 5 m length should also be taken into account.

5.1.2.4 Fascia, Soffit, and Bargeboard

The roof perimeter and eaves are among the most exposed parts of a building and are also difficult to access. Due to its lightweight nature and low maintenance needs, expanded PVC-U profile is also used in fascias, soffits, and bargeboards necessary to finish roofing systems. They are available in different colours, widths, thicknesses, and profile shapes. Soffits can be supplied incorporating venting slats. Appropriate trim sections are used for jointing or intersecting the profile. Fixing principles are similar to cladding. As with all expanded PVC-U materials, the only climate limitation is that they should not be installed where temperatures are above 50 °C.

5.1.2.5 Decking and Fencing

Vinyl decking, fencing, and railing are popular in the USA, and are available in traditional and innovative designs. The popularity of these applications is based on weatherability, durability, and minimum maintenance. The weatherability aspect takes account of the fact that fading will occur over time, but that fading will be uniform. Due to the designed method of fabrication, no surface screws, nails, or sharp edges show. The material is impervious to rock salt or other chemicals used for snow removal.

Vinyl decking has all the components of a wood deck, although its appearance is quite different from wood. Its overall smooth surface is etched to provide slip resistance and normal colour choice is between white, tan, or grey. Wood tones are also available. The possibility exists to more closely colour match the building's exterior finish. Decking is subjected to loading tests covering standard puncture, and blunt impact at low and high temperature. The plank system is also subjected to uniform uplift and download structural loading tests.

Vinyl deck planking can be cut using a power saw with a fine-toothed, tungsten carbide blade. The same tools that are used for wood materials are also used for vinyl fencing, decking, and railing. Typically installed on a wood substructure, planks are directly fastened by screws or clips.

Fencing systems can be designed to bend back into place or be quickly refastened. Standard testing includes tests that measure the vinyl fencing's ability to withstand cracking, impact under temperature extremes, warping, and discolouration. As with wood, vinyl posts are set in the ground with concrete. Fence rails can be attached to the posts by galvanised screws, hidden in the posts, or using a snap-in type system.

Vinyl railing is similar in appearance to metal or wood railing and is made in many different styles. Handrails must be designed and constructed to withstand a concentrated load (90 kg) applied at any point and any direction. Intermediate rails and panel fillers are designed to withstand a horizontally applied load of 22 kg on a 930 cm^2 area. There are also codes regarding height and spacing. Installation is carried out using galvanised steel post mounts bolted to joists at the rim and on the floor. Vinyl posts are then installed by sliding them over the post mounts. Reinforcement may need to be inserted into railing above certain heights.

5.1.2.6 Roller Shutters

Roller shutters, covering windows and doors, are used primarily to secure residential and commercial properties. In addition, they provide protection from the weather and give some degree of insulation against noise and energy loss. The shutter is based on extruded single- or multi-wall profile, which clips together and is rolled around a concealed roller when not in use.

5.1.3 Interior Construction Applications

5.1.3.1 Conduit and Ducting

Cable management systems utilise PVC-U pipe and profile for the safe and discrete trunking of electrical and data management cable. Various profile sections are available to retain the cable and to suit different requirements and most function on the basis of a lid that clips firmly into the profile section and conceal the cable. Conduit pipe can be cold bent, utilising bending spring which can be removed afterwards. Hot bending is required for pipe above 25 mm, using bending spring and a hot air torch. Corrugated conduit pipe is also available.

5.2 Design Considerations for PVC-P Materials

Due to the ability of plasticisers to influence the softness/hardness of articles and other possible formulation variables linked to many different forming and post-assembly techniques, the design possibilities for plasticised-PVC (PVC-P) are extensive and have already been utilised in many different applications.

5.2.1 Electrical Cable

The superior insulating properties of PVC-P linked to easier processability and greater durability has led to significant use of this material for insulation and sheathing/jacketing in many different electrical applications from building wire to fibre optic cabling. PVC-P is extruded over the conductor wire or insulated cable core.

Particular product characteristics to be considered include resistance to dampness and ozone, flexibility (including at low temperature), colour coding, weatherability, and fire performance. Electrical properties are, of course, critical. PVC-P has good dielectric properties, meaning that it can withstand relatively high voltages without breaking down. Its high electrical resistivity makes it an excellent insulator (see Section 4.5). PVC-P formulations, in this area, also take into account

possible abrasion during installation and for easy stripping from the conductor (typically copper but may be aluminium).

Typically, PVC-P is used in standard and low-voltage (<6 kV) and low-frequency applications with a continuous working temperature of 70–105 °C (depending on the formulation). Other polymers, particularly XLPE and polyvinylidene fluoride for insulation and PE for sheathing, have superior dielectric properties allowing use in high-voltage and high-frequency applications. They are also halogen free', which is perceived to be an advantage.

PVC-P electrical tape (thickness: 178 µm) is also supplied in a range of colours with a pressure-sensitive adhesive backing for wrap around insulation or sheathing, including the harnessing of wires and cables and general repair work.

PVC insulation and sheathing has widespread use in both domestic and industrial settings. It can be found in cables for power transmission, telecommunications, automotive cables, and harnesses, and in many different kinds of appliance wiring. Many different standards apply, including those from the International Electrotechnical Commission and Underwriters' Laboratories.

In the EU, all electrical goods must be supplied with an integrally moulded plug, to ensure that it has been wired up correctly and has the appropriate fuse fitted. PVC-P can be used in this application.

5.2.1.1 Fire Performance of Electrical Cable

Because fires can begin in electrical systems, the fire safety of wire and cable insulation and sheathing materials must be given a high priority in design and specification.

As explained in other sections, the high chlorine content of PVC makes it inherently more flame resistant than most alternatives used in electrical products. Although this effect is reduced due to the presence of plasticisers, this property can be enhanced by plasticiser selection and the incorporation of flame retardants and smoke suppressants. PVC-P cable will burn when exposed to a significant flame source (above 315 °C), but is slow to ignite and will typically self-extinguish when the flame source is removed.

The possible introduction of an acid fume test as part of fire safety testing under the EU Construction Products Directive could influence the future use of PVC in electrical cable (see Section 4.6.7).

5.2.2 Resilient Flooring

Resilient PVC-P flooring has become a valued design tool for many interior designers and architects. This can cover areas with heavy traffic use (contract flooring), sport and gym facilities, or in areas that must be kept clean (hospitals). There is also extensive use in residential areas. The material is available in different forms: cushioned (foam) flooring, solid sheet, and solid tile (may be self-adhesive).

A major aspect for vinyl flooring is its design flexibility. Virtually any look and style can be obtained to suit any decor due to the type of prints, finishes, and colours that can be achieved on the PVC substrate. The floor can be made to enhance the aesthetic features of the interior environment. Pattern and colour can be used to make a large room seem smaller or a small room more expansive. Hard surfaces can be mimicked, but with a warmer feel. Noise is reduced with a comfortable underfoot feeling.

Safety features, such as enhanced slip-retardant surfaces or control of build-up of static electricity, can be incorporated.

The role of vinyl flooring in healthcare facilities is also significant. Being almost impervious to water and having seams that can be sealed or welded, spills can be easily cleaned with disinfectant cleaners, leaving bacteria fewer places to hide and grow.

Some limitations as to its use apply. This can be in areas where heavy or sharp objects are dropped causing tearing, permanent indentation can occur from loads, or in outdoor installations where excessive heat and/or sunlight can cause distortion or discolouration. Damage can also occur from burning cigarettes, matches, or very hot items.

Different formulations and flooring construction are used for different applications. Test criteria cover the ability of the flooring:

- To withstand loads of different types – impact caused by momentary indentations, static loads, which are those that remain in a stationary position for long periods of time, and rolling traffic.

- To be resistant to stains and chemicals, appropriate to the situation.

- To reflect light to suit the illumination of the facility.

- To deaden noise in heavy traffic areas.

- To be safe from normal fire hazards.

The flooring is laid over a dry wood or concrete sub-floor, using a suitable adhesive. Seams can be welded or sealed for appropriate locations and flooring laid flush to the wall or shaped for a self-coving effect.

An alternative to vinyl flooring is linoleum, which is making a comeback, based on its perceived superior environmental credentials of renewable resources and biodegradability at end of life (see Section 9.4).

5.2.3 Wall Covering

Vinyl wall covering is also a valued design tool for many interior designers and architects. The reasons are both aesthetic and practical. A wide range of patterns, finishes, and colours are available for decorating almost every surface type. This, linked to enhanced durability of stain resistance, washability, and strength, has led to their popularity. In addition, they can be supplied pre-pasted in dry form, with the adhesive being activated in water.

An important factor has been new developments concerning photogravure and high-speed processing techniques.

Most wall coverings consist of three layers:

- The substrate or backing, which goes against the wall and is the carrier for the other layers. The backing can be a wide variety of materials ranging from woven and non-woven fabrics to lightweight paper.

The intermediate layer is vinyl and provides the surface upon which the decorative layer is printed. It also provides the background colour.

The decorative top layer, comprising inks and a protective coating, is applied to the intermediate layer. This is the thinnest layer and is usually the major reason why the wall covering was chosen.

There are several different categories of vinyl wall covering, each with specific performance characteristics.

Vinyl-coated Paper – a paper substrate coated with compact PVC. Classified as washable and strippable, it is resistant to moisture and suitable for residential bathrooms and kitchens.

Paper-backed Vinyl – with a thicker vinyl sheet, applied via a plastisol coat onto paper, this wallpaper is classified as scrubbable (in its compact form) and peelable. It resists moisture, stains, and grease and can be used in most areas in the house or business. The vinyl coating can be compact (with or without embossing), expanded (either during the hot embossing stage or chemically), or textured foam (either self-coloured or paintable). The blown vinyl' gives a three-dimensional effect and is good for covering imperfect walls, but it is not suitable for areas requiring regular cleaning.

Fabric-backed Vinyl – a compact vinyl intermediate layer laminated to a woven or non-woven fabric substrate. The vinyl layer thickness can vary to suit the intended end use. The woven fabric can be scrim. The non-woven fabric is produced from cellulose pulps and textile fibres, combined with binders and reinforced with acrylates. An alternative construction is a solid or expanded vinyl layer, coated onto a non-woven tissue substrate, which gives dimensional stability. This allows direct application to the wall in a paste-the-wall concept. This type of construction is considered more breathable, i.e., allows water and air to pass through and so helps to reduce mould and mildew problems in warm, humid conditions. The incorporation of a microbiocide in the PVC formulation will also assist.

5.2.4 Roofing Membranes

PVC roofing membranes are based on single-ply technology, utilising PVC-P, for commercial and industrial buildings with low-slope roofs. Obviously, they must be designed to withstand wear and tear in the toughest of weather conditions and remain watertight over many years. Flame resistance is also an important factor. Cost effectiveness and low weight are other factors.

Vinyl roofing membranes are typically light coloured and hence tend to reflect heat away from the rooftop and so reduce the amount of heat that enters the building. This can assist in reducing the operating cost of air conditioning. Patterns, logos, and colour variety can be incorporated to match particular design requirements. Membranes are designed to repel dirt, maintaining aesthetic appeal and maximising reflectivity. The internal reinforcement fabric is usually based on woven polyester or fibreglass.

Vinyl roofing membranes can be designed to resist wind uplift, structural movement, and harsh outdoor elements. They are formulated for good low-temperature flexibility and high-temperature tolerance. Membranes are usually sealed by overlapping, using hot air to weld the joints giving a permanent and watertight seal. Many different roofing types can be accommodated, such as barrels, domes, steep slopes, and large expansive flat roofs.

There are three main fastening techniques to suit roof pitch and design. These include mechanical fastening, adhesion bonding (using water-based or low solvent-based adhesive on both the substrate

and the membrane), and use of ballast such as stone, concrete, and so on. The adhered system is installed directly over a rigid insulation board that has been fastened to a suitable substrate.

Vinyl membranes can also be used to re-roof and re-cover existing roofs.

Another application is in temporary or permanent inflatable buildings for sports halls, warehouses, and so on. The membrane construction can be specifically designed for this application.

5.2.5 Coated Metal

Aluminium or steel coils can be spread coated with a PVC-P protective and decorative surface. This application has a proven history with the PVC-P coating giving excellent flexibility and high impact and chemical resistance, linked to good weatherability. Different colours and embossed finishes are used to give distinctive features. The coated sheet material is supplied in coil form for subsequent use by cutting and forming into facades or roofing sheets. PVC-P is very cost effective in this role and eliminates the need for painting and maintenance.

Fencing and street furniture signs can also be coated to give high-gloss and weather-resistant finishes.

5.2.6 Toys and Baby Care Items

PVC-P formulations can be adjusted to give the exact performance and quality requirements for many different type of toys, such as dolls, bath toys, inflatable paddling pools, balls, and so on. Still retaining their cost competitiveness, various production techniques are available for conventional toys and toys designed to meet new trends, film merchandising, and so on.

Important aspects are the bright colours that can be achieved, the different shapes available from different moulds, flexibility, and easy assembling techniques. Vinyl-coated fabrics can also be printed with suitable designs. All vinyl materials, toys, teethers, and so on, can also be kept clean and hygienic.

However, it should be noted that there is still considerable political discussion about the safety of the phthalate plasticiser diisononyl phthalate used in toys and baby care items (see Section 9.2.3.1). The European PVC industry, in particular the European Council for Plasticisers and Intermediates, is contesting the proposed ban which has ignored the EU risk assessment results.

5.2.7 Safety and Personal Protection

5.2.7.1 Buoys and Fenders

Rotationally moulded PVC-P has uses for flotation devices, such as buoys and fenders, due to the shapes and bright colours that can be generated.

5.2.7.2 Rainwear, Aprons, and Gloves

Spread-coated PVC-P has another well-proven application in heavy-duty or domestic use, in rainwear, aprons, and gloves.

Rainwear can be made as functional or fashion dress items, in bright solid or subdued semi-transparent colours with suitable flashing.

Aprons and tabards are designed for both domestic and commercial use, with attractive designs, which are fun to wear and easily wiped clean. They can also be machine washable. Safety aprons are also manufactured to protect the wearer when using knives, hazardous materials, and so on.

Safety gloves, which can incorporate improved grip properties due to an external coarser surface finish, also utilise PVC-P on a cotton liner. The process allows a variety of colours, sizes, and lengths in different formulations to suit exposure to different materials (oils, fish, and so on).

5.2.8 Automotive and Transport

5.2.8.1 Interior Trim

PVC-P is used extensively for the interior trim of cars and light vehicles. This is due to its aesthetic leather-like appearance and feel, with good scratch resistance. The PVC-P must be formulated to meet the specifications of the different automotive suppliers.

Dashboards and armrests are moulded items, with door panels being made from expanded or compact PVC-P coated onto synthetic fabric or cotton. The coated fabric permits the use of lower cost manufacturing methods for assembly. Colour, texture, and feel can be made to suit the required design.

PVC-P plastisols are also used for the manufacture of automotive component covers, gear lever bellows, hand grips, cable shrouds, gaiters, sleeves, and end caps in brightly coloured and high-gloss dip mouldings.

High-density PVC-P sheets are very effective for sound insulation and are used to keep the inside of the vehicle quiet (from engine or exterior noises). They are formed to the shape that they are required to fit.

5.2.8.2 Exterior Automotive Protection and Trim

PVC-P is used for underbody protection due to its waterproof qualities, good adhesion to steel, and resistance to impact from stones, and so on, on roads. Its application and subsequent gelation also fits with the paint spraying and low-temperature drying ovens.

Both PVC-U and PVC-P, with or without glass fibre reinforcement, can be used for decorative and protective profile. The design is created to suit the overall flow lines and colour of the car.

5.2.8.3 Tarpaulins

PVC-P-coated polyester fabric is ideal for tarpaulins for covering trucks, and so on, due to good weathering properties and dirt resistance. Colour can match the designers' scheme with logos and company information easily applied.

5.2.9 Advertising Banners

Many advertising banners are based on PVC-P-coated fabric, due to various attributes linked to printability in any eye-catching colour or design, lightweight construction, and durability.

A more recent development is based on using vinyl mesh for building wraps. Utilising digital imaging technology, huge images can cover buildings with photographs, advertisements, or murals. Again, this use is based on ease of printability and ability to withstand different weather conditions.

Reference

1. *PVC Pipe Systems Manual*, joint publication between WRc plc, Swindon, UK and the BPF, London, UK. Available free online (*www.wrcplc.co.uk/pvc*).

2. L.R. Holloway in *Proceedings of the PVC 99 Conference*, Brighton, UK, 1999, p.92.

6 Processing of PVC

The intimate mixing of polyvinyl chloride (PVC) resin with appropriate additives is necessary prior to converting it into a thermoplastic melt.

6.1 Dry Blend Mixing

Dry blend mixes are powder compounds resulting from the blending together of primarily suspension-PVC (S-PVC) resin together with the other formulation ingredients.

6.1.1 High Intensity

Batch high-speed mixing, followed by a cooling stage, is the most favoured process to produce unplasticised-PVC (PVC-U) and relevant plasticised PVC (PVC-P) dry blends at high outputs. The process is as follows:

• Raw material storage and supply of all formulation ingredients to the mixer.

• Dosing and spraying of all the ingredients (appropriate for the product form and weight loading), in the correct order if necessary, into the mixer. This can be semi- or fully-automated.

• Mixing (a two-speed operation may be used) to the correct temperature by which time mixing has been completed. This is normally automatically controlled.

• Discharge from the hot mixer, through a filter mesh if required, into the cooler mixer.

• When the dry blend is sufficiently cool, it is discharged via a filter to remove oversize particles. Suction stream or screw conveying is used to transport the dry blend to the feed stations for processing.

Other important criteria also have to be considered for the dry blend mixing stage and subsequent transportation to the processing equipment:

• Dry blend homogeneity and consistency.

• Free-flow ability.

• Bulk density.

• Ease of handling and storage stability.

High-intensity mixers are vertically mounted cylindrical bowls, of volume varying from 40 to 2000 litres, with the mixing tool (propellers or knives) base mounted on a mixing shaft and a top deflector to redistribute the material. Tool blade designs vary depending on the manufacturer. Tool speeds

of 300 up to 1500 rpm are used, depending on the motor drive and bowl volume. A deep vortex is created to allow the material to be constantly rotating within the bowl and thus there is an optimum mixer loading to achieve this effect. Under the effect of primarily frictional heat, the temperature rises, allowing the absorption of the liquid and low-melting solid components. Further mixing ensures that the non-melting components are efficiently dispersed (in some cases fillers and certain pigments are added just prior to reaching the final mixing temperature). The hot mix (now around 110–130 °C) is transferred to a much larger (twice to three times the volume of the intensive mixer) water-cooled, low-intensity mixer until a temperature of ~50 °C is reached. The aim is to expose the dry blend to as much effective cooling surface as possible. This results in reduced agglomeration and improved free-flowing properties (by reducing electrostatic charges).

PVC-P formulations take longer to mix due to the time necessary for plasticiser absorption to occur.

The removal of dust and fumes from the workplace is also necessary for such installations.

Batch monitoring and verification of composition procedures should also be in place. Motor load amperage and mixing temperature increase are also good records of the mixing process, particularly for the plasticiser absorption phase.

6.1.2 Low Intensity

Virtually shear-free, low-speed horizontal mixers offer gentler product handling with a uniform distribution of all ingredients, with no change in particle identity. The mixer walls, jacketed for heating and cooling, carry the bulk material back into the centre. This produces continuous dividing and reuniting of the material. Centrifugal forces are sufficient to throw material particles into free space where they collide with other particles. This breaks up agglomerates. Normally, this technique is used for cold mixing and by heating to aid plasticiser absorption.

Types of mixers are U-shaped troughs with either helical ribbon or paddle agitators. The helical blades are designed with the outer ribbon moving material towards the centre and the inner ribbon moving the material towards the wall. The ribbon also rotates at between 25 and 75 rpm to move the material both radially and laterally. Paddle agitators are an alternative, with the paddles positioned to move materials in opposing lateral, as well as radial, directions.

6.2 Liquid PVC Blending

Plastisols are essentially liquid dispersions of non-absorbent (at ambient temperature) spherical particles of emulsion or emulsion/microsuspension PVC resins in plasticisers. Other additives such as heat stabilisers, viscosity control agents, and so on, are also necessary. The resulting product is a flowing liquid or paste-like material.

The mixing process is critical in order that the PVC agglomerates (between 10 and 50 µm) are broken down. The finished plastisol contains a mixture of particles and agglomerates varying between 1 and 20 µm. The plasticiser penetrates the agglomerates during mixing and gives a lubricating coating, so allowing them to move against each other. This in turn allows the agglomerates to break up and release air.

Mixing temperatures, generated by friction, are normally in the region of 35–45 °C. As the temperature increases, the plasticiser viscosity decreases which also assists the wetting of the particles.

Mixers consist of mixing blades that are raised and lowered into the mixing bowl. The types of mixers used are:

- High-speed dispersion vertical mixers, which are fitted with a variable speed drive and a toothed disc at the end of the vertical shaft. This type suits the lower viscosity plastisols used in wall and floor coverings.

- Lower-speed planetary mixers are fitted with vertical trellis-type paddles, which rotate around the drive access in a circular motion, while orbiting around the mixing bowl. The paddles continually advance around the wall of the bowl, removing material and transporting it to the interior.

There may be a two-stage mixing procedure used where all the solids are dispersed in part of the plasticiser. The remaining plasticiser is added at the second stage, thereby improving plastisol mixing. This type of mixer requires longer mixing times but is suitable for high-viscosity pastes with very little friction being developed in the process.

All mixers are usually enclosed and fitted with a vacuum de-aeration facility, particularly necessary for transparent topcoat and foam formulations.

6.3 Gelation

In the case of PVC plastisols, gelation occurs on the basis of heat imparted to the material during the processing stage (above 150 °C). As the temperature rises, absorption of the plasticiser causes the resin particles to swell and coalesce, solidifying the plastisol. A further rise in temperature leads to full fusion, so that on cooling the composition gains optimum mechanical properties. Gelation has been shown to occur in several steps (as explained in Section 3.2.2), depending on the speed of dissolution of the PVC particles. A higher concentration of plasticiser requires a higher gelation temperature. Other influences are the solvating power of the plasticiser and K value of the PVC.

For dry blends, melt compounding is required to give the thermomechanical energy necessary to achieve interdispersion down to microscopic and possibly intermolecular level. A high level of mechanical heat is generated due to heat input and shear generation and it is now generally accepted that the gelation mechanism involves compaction, densification, fusion, and elongation followed by melting. Much work in this area has been carried out at Loughborough University by Professor Gilbert and her team where relevant papers can be sourced (*www.lboro.ac.uk/departments/iptme*).

The gelation or fusion level is associated with the degree of destruction of the inherent particulate boundaries of the PVC grains and the subsequent merging of the primary particles and aggregates. In addition, there is an extensive network of interconnecting crystalline regions that develop with increased processing temperature. This degree of fusion and the extent of crystallinity that exists within the polymer network are essential to achieve the finished product quality and properties, the crystallites acting as crosslinks in a three-dimensional network. It seems that there is an optimum level of gelation for a particular product and/or process method.

Several different gelation measurement methods have been described in the literature, particularly differential scanning calorimetry. In addition, capillary rheometry, transmission electron microscopy,

and atomic force microscopy have also been studied. Gelation level is characterised either by crystallinity-related aspects or factors that relate to the development of the three-dimensional network and the corresponding disappearance of the particulate structure [1, 2, 3].

Another technique is based on solvent absorption usually involving methylene chloride and visualising swelling and solution effects.

6.4 Melt Processing

PVC, being an amorphous polymer, has a lower specific heat capacity than semi-crystalline polymers. This means that the energy required for softening the resin will be lower, i.e., less costly melt processing. Similarly, the amount of heat to be removed during cooling after melt processing is less. Another positive point is reasonable melt elasticity and good melt strength, which allows the use of PVC in many different melt processing techniques. Die swell is also relatively low (die swell results as the polymer melt emerges from the die and is a function of the elasticity).

However, these benefits must be set against the high melt viscosity and process heat stability limitations of this material.

6.4.1 Melt Compounding

For certain operations or scale of operations, the dry blend is fed directly into the processing equipment, e.g., pipe and profile extrusion, which obviously includes the melt compounding stage.

For some processes or smaller scale operations, the dry blend (PVC-U or PVC-P) must be gelled/melt compounded, usually into a pellet or dice product form. This may be necessary for the type of processing equipment used for shaping the material, e.g., calendering, or where a high degree of homogenisation is required to achieve the performance requirements of the final product. Continuous melt compounding extruders are now the favoured option based on:

- Counter-rotating (i.e., in opposite direction) twin screw as explained in Section 6.4.2.1.

- Co-rotating (in the same clockwise or anticlockwise direction) twin screws with kneading elements. The barrel is in segments and the length is determined by the process needs, with the screws designed to include mixing, conveying, plasticising, and homogenising.

- Oscillating kneader extruder, based on a single helical screw blade which, in addition to its rotary motion, also makes a reciprocating axial movement. In one complete turn of the screw there is one forward and backward motion. Kneading teeth or pins are mounted on the barrel, which is hinged for easy access, and the material is sheared in the shear gap between these teeth and the screw flights. This technique is reputed to give maximum mixing performance with relatively low energy consumption. In addition, the design of the kneader barrel and screw gives a self-cleaning or wiping capability.

A twin-screw feeder unit is used to dose dry blend into the compounder. A discharge screw feeds the melt into a pelletiser unit, which is a multi-hole die plate through which the melt is forced into strands, cut by rotating knives, and cooled.

6.4.2 Extrusion

6.4.2.1 Twin-Screw

Almost exclusively used for extrusion of PVC-U into pipe, profile, sheet, and compounds (including flexible), extrusion equipment consists of a cylindrical barrel containing two close-fitting, intermeshed, counter-rotating Archimedean screws. Low shear processing and venting capabilities are key features of twin-screw extruders. Venting is carried out under vacuum (degassing) to remove volatile components at the appropriate fusion stage.

PVC dry blend is fed in via a hopper at the start of the screws and is conveyed forward, softened, sheared, and finally gelled by rotation of the screws and the heat of the barrel. The resulting homogeneous viscous melt is forced through a heated die fitted to the exit end of the barrel. Thereafter the downstream equipment sizes or calibrates, cools, and pulls off the product which is also cut to desired lengths.

The heated screws rotate in opposite directions (one screw clockwise, the other screw anticlockwise) to each other and perform three basic functions, feeding, gelation, and metering, with the screw flights designed accordingly. Venting is incorporated to remove entrapped air and volatiles. The barrel is temperature controlled, usually in different zones along the length.

The concept of twin-screw extrusion is short residence time in order to minimise thermal degradation, linked to high output. Screws are typically nitrided, molybdenum plated, and/or chromed to protect against acid corrosion, abrasion (primarily from the filler), and contact with the barrel wall. Barrels are internally lined with various high-alloy nitrided steels.

Screw design is complex, but enables the melt temperature (which can be in the region of 190–200 °C) to be controlled more accurately. Screws are categorised by the ratio of their length to depth (L/D ratio) and have been 22:1 (22D) and 26:1 (26D). New 36D extruders have also been introduced which are claimed to have higher output in combination with less wear.

Dry blend can be fed into the extruder either by flood or doser feeding, determined by the dry blend flow characteristics, packing density, and output requirements. Flood feeding is obviously the preferred option.

Two main types of screw design are used, i.e., conical and parallel. Conical twin-screw extruders have two intermeshing screws which together form a cone shape (see **Figure 6.1**). These screws are shorter, with larger diameter shafts than parallel screws. Screw deflection inside the barrel is reduced and as a result this extends the life of screws and barrel. The feeding zone offers more surface area allowing faster and
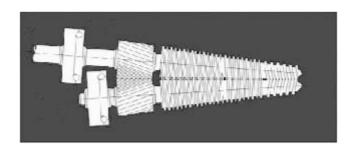
Figure 6.1 Conical twin screws. (Source: *http://plastics.milacron.com*)

more uniform heat transmission. Thrust bearings are much larger than with parallel screws. A smaller exit diameter lowers rotational shear and reduces back thrust, while increasing pumping efficiency.

Conical twin-screw extruders are usually used for low to medium output ranges. Later developments have focused on increasing output by increasing screw flight depth, particularly at the metering zone.

Parallel twin-screw extruders have two intermeshing parallel screws with higher output capability, due to higher torque power input. A wider processing window is also believed to be a feature.

A useful review of the twin-screw extrusion process has been presented [4].

6.4.2.2 Single-Screw

Single-screw extruders are fed by pre-gelled compound in solid pellet form or powdered PVC dry blend (primarily flexible). These are conveyed along a flighted screw enclosed in a heated barrel.

Screw design is based on three functions, starting at the feed zone: (1) compacting and conveying towards the (2) melting section under the action of shear against the barrel wall and (3) metering or pumping into the die.

Single-screw extruders develop more frictional heat and rely more on back pressure from the die to improve homogeneity. Screw design involves higher compression ratios, e.g., 2:1, which means the volume occupied between two flights at the start of the screw is twice that occupied between two consecutive flights at the end of the screw. The L/D ratio is typically 24:1.

PVC-P applications, such as wire and cable, glazing strip, profile, tubing, hose, and so on, run on single-screw extruders which are fed by gelled compound.

6.4.2.3 Co-extrusion

Co-extrusion permits the simultaneous capping of a specially formulated layer or layers of PVC (or alternative material) on to the bulk material, normally pipe or profile. The specially formulated layer is normally virgin PVC to cap lower cost virgin or regrind or foam to give good gloss, a particular colour and surface finish with good weathering performance, if necessary. The process can also be used to co-extrude gasket directly on to window and door profile [5].

6.4.2.4 Foam Extrusion

PVC-U foam extrusion has been known since the 1960s, but more rapid development has taken place due to improved specialist machinery and techniques. Additional benefits to those associated with solid PVC are weight and cost savings. Two processes are possible: (1) free foaming where the blowing gas freely expands in the melt extrudate as it leaves the die going into the calibrator; and (2) inward expansion (Celuka process) where the extrudate is fed on to the calibrator walls via a die mandrel, the torpedo creating a space into which the extrudate expands. The die and calibrator are the same size and this process creates its own skin on the extrudate surface.

Free foam extrusion may also have a skin co-extruded on to the surface as the inherent surface skin is very thin by this process.

6.4.2.5 Extrusion Tooling

There can be many different components in the extrusion tooling section between the end flange of the extruder barrel and the die. A breaker plate gives the seal between the barrel flange and the adapter. The adapter adapts the thermoplastic flow into the die system, which will have lead-in channels to streamline the flow into the final shaping process at the die lips. The breaker plate can hold screens or screen packs of differing mesh size to filter out contamination. They also create back pressure to assist with homogenisation.

Die design is critical to the extrusion process and material rheology and flow through the die, once ascertained on a trial and error basis, can now be investigated using techniques to determine shear viscosity and slip viscosity. Computer-aided design systems, linked to flow and cooling simulation and a database of rheology and physical properties, are being applied to die design, particularly profile. The complex behaviour of PVC during the extrusion and die forming process can be computer modelled, with many potential changes being quickly evaluated.

6.4.2.6 Downstream Equipment

Profile forming is achieved by passing the extrudate through a series (up to three) of 'dry' calibration tools, which cool the material through contact with metallic walls of the calibrators. Vacuum holes or slots are used to improve contact with the water-cooled walls and maintain final product dimensions. Alternatively, improved and more even cooling by direct water contact is achieved with vacuum tank calibrators, with flooded profiles and support discs. The supporting discs scrape the water off the profile surface and this gives a good heat transfer. There is only need for one dry calibrator (so less expensive) in this process.

Vacuum tanks, with spray cooling, are common for pipe extrudate. The material is vacuum sized and subsequently cooled with water by total immersion or spray.

The extrudate is transported away from the calibration unit by a belt haul-off, the speed of which is linked to the extrusion speed. The final operation is the in-process cutting to length.

The complete extrusion process is now automated, via computers, for the control of speed, temperature, melt throughput, weight or thickness tolerance, and documentation.

Some pipe systems are supplied with push-fit elastomeric sealing ring joints, integrally formed with the pipe. This is carried out by heating plain-ended pipe, reshaping, and expanding locally to form a socket. The expanded shape is then cooled with the sealing ring fitted automatically during the forming operation, or as a post-forming operation.

Corrugated pipe, primarily used in land drainage, is produced using thin-wall extrudate which feeds into a corrugator system based on mould blocks transported along tracks. Vacuum is also used to take up the corrugated shape. Sheet and film extrusion lines include cooling and polishing rolls.

6.4.2.7 Plate-out

Plate-out is a particular problem for PVC extrusion and is the formation of undesired deposits within the extrusion process, components of which are screws, die, calibrator, and so on. Plate-out

is usually caused by incompatibility within, or reactions resulting from, the formulation ingredients in combination with processing conditions. The mechanism for plate-out formation has been studied [6] and attributed to:

- Separation of PVC-incompatible, volatile materials in the de-gassing zone, which condense in cooler regions.

- Excess external lubricant forming a phase with calcium stearate, which coats inorganic ingredients (stabiliser, filler, and titanium dioxide). These particles migrate to the region between the metal and polymer melt and become trapped in regions of compression and decompression. The liquid phase continues, leaving behind the inorganic particles which stay and initiate a further build-up. Moisture in the die, which is not removed, also encourages this mechanism (the Lippoldt mechanism).

- Moisture also plays a substantial role in the formation of plate-out in the calibrator. Water-insoluble substances, with boiling points well above 100 °C, are ejected by steam into the gas phase. Remaining water originating from lead stabiliser system is not removed and is heated under pressure in the extruder to the mass melt temperature. With the pressure outside the extruder being much lower, the steam escapes and carries with it formulation ingredients so that a layer of coating settles in the calibrator.

- The limited solubility of various organic substances in the polymer melt also plays a part. When the melt passes into the calibrator, the mass temperature is reduced rapidly and with it the solubility of the ingredients. There is a build-up of heterogeneous phases as in the Lippoldt mechanism, one of which can precipitate between the cold calibrator and the extruder.

6.5 Injection Moulding

Injection moulding of PVC-U articles is confined to relatively simple shapes, due to its viscoelastic nature and process heat stability issues. Melt temperatures of between 170 and 210 °C are necessary.

Injection moulding is a discontinuous process that produces articles in their final shape. A mobile reciprocating screw, within the heated barrel of the machine, gels, transports, and forces the hot material via channels or runners, sprues, and gates through a nozzle and into the mould cavity. The mould, which is in two halves, is maintained at a specific temperature (fixed between 20 and 60 °C) and is clamped under a specific pressure load. After cooling, the clamping unit is opened, the two mould halves separate, and the part is ejected. The waste material, such as runners and sprues, is granulated for reprocessing.

The relatively high melt viscosity and potential thermal degradation of PVC requires close attention in relation to temperature, shear conditions, and flow geometry. The most important stages of the process are melt preparation and mould filling to minimise shear heating caused by excessive back pressure, screw speed, or injection rate. Screw and mould designs have made big advances. Screw-tip cooling is recommended, as this is where the material is at its hottest. Screws with a compression ratio of 2:1 and an L/D ratio of 18:1–24:1 are common (particularly if moulding directly from dry blend). Chrome plating is essential to protect the components from HCl. Mould shrinkage can be 0.3–0.5% depending on the article.

PVC-U applications, usually based on lower molecular weight polymer, cover the construction and telecommunication areas.

PVC-P material is easier to mould but mould shrinkage can be higher (above 1%). PVC-P applications are footwear, automotive, medical, and electrical, including complex shapes and thin-walled items.

Strains imposed on the material during injection can result in residual stresses causing undesirable shrinkage, sinks, and surface defect formation.

6.6 Extrusion Blow Moulding

For thin-walled containers, PVC-U gives a combination of high clarity, inherent rigidity, and good barrier properties. However, the use of PVC in this area has greatly decreased due to the changeover to polyethylene terephthalate for cost-effectiveness reasons.

Extrusion is mainly by a single-screw horizontal machine which changes to vertical flow via a 'swan neck' arrangement. Air is fed to the centre of the parison.

In the stretch blow moulding process, which is the most common, the extruded parison is initially blown undersized, and then stretched and blown to its final shape in a second mould. This produces biaxial molecular orientation of the container walls, which improves impact resistance, rigidity, and clarity. However, permeability is reduced.

6.7 Calendering

A calender is essentially a set of four very large steel rollers mounted in a cast iron frame, usually in an inverted L-shape, in such a way that they can be rotated, and the distance between each pair of rollers adjusted. Consecutive rolls squeeze the material resulting finally in a continuous sheet of the desired thickness. PVC, ranging from rigid to semi-rigid to flexible, is produced continuously in film or sheet up to approximately 1.5 mm in thickness and up to and over 2.0 m in width.

Calendering is much more capital intensive than the extrusion process, but higher production rates and more accurate product thickness are obtained. Mini calenders or Calandrette® lines are available for the production of rigid and semi-rigid PVC films with lower investment costs.

The calender rolls have to transmit heat evenly across the face and need to be independently variable in speed so that friction between two adjacent rolls can be applied. The surfaces of the rolls need to be contoured to an accuracy of a few micrometres to ensure even film thickness in both lengthwise and crosswise directions. The surfaces of the final two rolls can also be textured, ranging from highly polished to heavy matt, depending on the sheet finish required. Hot melt is generated through a continuous extruder compounder feeding into the intake nip of the calender. Alternatively, an intensive internal mixer can be used consisting of two heavy-duty tear-drop-shaped counter-rotating rotors in a heated chamber, based on a batch process, feeding on to a two-roll holding mill.

The passage of hot melt between the rolls creates a pressure forcing them apart. There is a rolling bank of feed material created in the gap or 'nip' set between the first pair and also the second pair of rolls. Passage of the material is controlled by roll temperature, surface finish, and the ratio of the roll speeds at the nip. The final calender nip controls film thickness.

The hot sheet is drawn from the final roll by stripper rollers that can be temperature controlled to permit gradual cooling, and regulated rotationally to allow stretching to the required dimensions.

In-line embossing can be carried out by feeding the hot sheet between a heated embosser and rubber back-up roll. Final cooling is achieved using water-cooled drums.

Plate-out can also be a problem in this area due to the formation of coatings that adversely influence sheet quality.

Typical applications for PVC-P materials include floor and wall coverings, film packaging, decorative surface coatings, and stationery. Calendered PVC-U sheet is used for thermoforming of packs and containers.

6.8 Plastisol Moulding Processes

PVC plastisol compounds can be manipulated into shapes, or applied to fabrics in the ungelled state by either simple flow techniques or by very low-pressure processes. The main techniques are spreading, dipping, spraying, and rotational and slush moulding.

6.8.1 Rheology

An understanding of the rheological behaviour is necessary, as most PVC pastes are classified as non-Newtonian liquids and can be dilatent (shear thickening), pseudoplastic (shear thinning), or thixotropic (viscosity reduces with time under constant shear). Each process technique requires specific rheological characteristics to suit the process. This is achieved by appropriate formulation based on the PVC grades developed for the process and knowledge of the influence of shear rate and time under constant shear.

Newtonian flow behaviour is also possible with some specific paste PVC grades.

6.8.2 Spreading or Coating

For the coating of continuous substrates, such as flooring, wall covering, and tarpaulins, direct or transfer coating is used. The paste can be applied directly using knife on roller or belt, or indirectly via reverse roll coating. The substrate can be a carrier material that is removed later. This process permits multi-layer coatings, including foam, and embossed finishes to be carried out in line. The final process involves pregelling and gelation in a continuous oven.

Screen coating, typically used for wall coverings, relies on plastisol being pumped into a cylindrical metal screen with fine perforations. The paste is forced through the perforations via a rubber blade on to the substrate - the amount deposited is controlled by the screen mesh size and rubber blade pressure and angle.

A coating installation can consist of up to three coating heads whereby up to three layers can be applied in a single-step process. One of these can be a foam layer, where a blowing agent is activated to decompose with gas generation. Chemical embossing, to give a sculpted effect, can be achieved by incorporation of an inhibitor into the print design layer. This prevents the activation of the blowing agent in those areas.

Coil coating, usually on metal, is carried out using a roller with concentric grooves, with the depth of the grooves determining the coating weight.

6.8.3 Rotational, Slush, and Dip Moulding

Rotational moulding is carried out using closed moulds that undergo rotation through 360° in three dimensions after feeding in a fixed quantity of paste. The rotation ensures that the paste is evenly coated over the mould interior. The moulds are fed through an oven where the paste is gelled and fused. On cooling, the article is peeled from the mould, which is designed to split open. This process is very flexible and allows the manufacture of very small parts (e.g., parts for small toys) through to large parts (e.g., tanks and containers). Automotive armrests and dashboards are also made by this technique.

Slush moulding utilises heated open moulds which are inverted to remove excess plastisol. Layer thickness is controlled by the rheology of the paste, timing, and temperature. Consecutive layers can also be built up in this process. Typical products made by this technique are PVC-coated flexible foam for automotive trim or boots.

Dip moulding utilises a pre-heated former which is dipped into the paste and withdrawn at a constant rate. After heating in an oven and cooled, the article is peeled off the former. Disposable gloves are manufactured by this process.

6.9 Powder Moulding Processes

Powdered materials can also be processed by rotational moulding and slush moulding techniques to give PVC-P articles.

Powder moulding processes can be used for metal treatment to give protection against corrosion and for aesthetic reasons.

6.9.1 Fluidised Bed

The fluidised bed consists of circulating a gas upwards through a layer of solid PVC particles lying on a porous grid inside a column. The treated object to be covered is pre-heated to about 350 °C and immersed in the fluid bed for a very short period to allow the PVC to coat it. After cooling, an oven annealing process may be carried out to smooth the surface.

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7 Property Enhancement of PVC

The history of polyvinyl chloride (PVC) formulating is based on enhancing the properties derived from the starting raw material. The influence of impact modifiers and plasticisers has already been covered. This chapter focuses on work carried out to expand PVC, a so-called commodity plastic, into the property performance areas given by some engineering plastics, such as acrylonitrile–butadiene–styrene (ABS), and so on.

7.1 Crosslinked PVC

Crosslinking of PVC results in the improvement of a number of properties, particularly at elevated temperatures. Investigative work has been carried out on both unplasticised-PVC (PVC-U) and plasticised-PVC (PVC-P) formulations.

7.1.1 Chemical Crosslinking

Chemical crosslinkable formulations need to generate a sufficient crosslinked portion or gel content (up to 50%) with satisfactory processing stability (usually a conflict) and should not, of course, crosslink during processing. Crosslinking is achieved hydrolytically.

For some PVC-P formulations, mercaptosilanes and aminosilanes grafted by nucleophilic substitution during processing appear to be more suitable than organic peroxides in achieving improved solvent and abrasion resistance [1, 2].

Organic peroxide crosslinking of PVC foam formulations (based on emulsion-grade resin) has shown the positive benefit of a trimethylolpropane trimethacrylate (TMPTMA) compound as co-agent, with good thermal stability and a very dense crosslink network. In the presence of the peroxide, radical reactions occur and the TMPTMA is grafted onto the PVC chains with a resultant network formation [3].

The use of a reactive plasticiser, triallyl cyanurate, has also been shown to improve the high-temperature creep resistance of organic peroxide-crosslinked plastisols [4].

The chemical crosslinking of PVC-U formulations is considerably more difficult due to the fine balance of achieving a sufficient level of crosslinked polymer, adequate thermal stability, and the avoidance of premature crosslinking during processing. This has been investigated with successful results from aminosilane and peroxide/TMPTMA crosslinking systems, with slower crosslinking attributed to the reduced diffusion of water required to hydrolyse the silane. Thermal stability still has to be improved [5]. The peroxide crosslinking system has shown gel contents of 30–40% with improved mechanical properties using appropriate curing agent levels.

7.1.2 Irradiation Crosslinking

Irradiation crosslinking of PVC-U carried out over a dosing range of 20–200 kGy using an electron beam has shown a marked increase in glass transition temperature (T_g) in the presence of trimethylolpropane triacrylate (TMPTA), with minimal thermal degradation [6]. Electron beam irradiation has also been investigated on a PVC-P wire coating formulation, in the presence of different reactive monomers including TMPTA and TMPTMA, with the influence on different properties observed [7]. Flame retardancy of PVC-P formulations for wire and cable has also been improved using TMPTA and irradiation doses of 90 and 120 kGy with the incorporation of appropriate flame retardants [8].

7.2 Orientation

The mechanical properties of PVC-U can be improved substantially by stretching the polymer, usually in both directions (biaxially) but may be in one direction (uniaxially), at temperatures above T_g. In addition, material costs are reduced. Uses to which this process can be applied are pipe and sheet.

7.2.1 Pipe

As already indicated in Section 5.1.1.2, pressure pipe design, based on conventional PVC-U, has to take account of a higher safety factor. This is due to the more brittle nature of PVC pipes in comparison to polyethylene (PE) and therefore having a greater risk of not performing to their strength potential. If the ductile balance between strength and toughness could be changed to increase ductility, then a lower safety factor could be used [9].

Biaxial PVC has both higher strength and toughness, probably justifying a lower safety factor. However, the strength gains with oriented PVC are such that pipe stiffness limitations could be breached. This is a limiting criterion for strong materials where the pipe wall would be so thin as to allow deformation of the pipe. Thus, the safety factor of two has been maintained. Similarly, there is a limit to the strength that can be usefully exploited.

Table 7.1 shows the relationship between standard dimensional ratio (SDR; ratio between outside diameter and wall thickness) and stiffness for standard PVC-U and a biaxial PVC with a long term-strength of 40 MPa and a safety factor of two. These values apply for a 1 MPa pipe.

A stiffness value of 4 kPa is the minimum allowable value in CEN pressure standards. In **Table 7.2** it can be seen how strength and safety factor may be combined while still meeting the stiffness criterion.

Table 7.1 Relationship between SDR and stiffness for PVC-U and biaxial PVC			
Material	**Long-term strength (MPa)**	**SDR**	**Stiffness (kPa)**
PVC-U	25	26	20
Biaxial PVC	40	41	6

Table 7.2 Operating pressure and stiffness values for a combination of long-term creep strength (LTS) and safety factor				
Minimum required strength (MRS) (MPa)	Safety factor	SDR	Pressure (MPa)	Stiffness (kPa)
40	2	41	1	6
50	1.6	41	1.6	6

The process can be continuous and is essentially the extrusion of a thick-walled preform, which is stretched to produce a biaxial pipe. The key to the process is the mandrel over which the pipe is expanded, being hot and lubricated at the front end to facilitate the stretching process in the hoop direction. The orientation is frozen in at the back end of the mandrel which is cooled. A second calibration stage controls the outside diameter.

Molecular orientation introduces anisotropy into a material. This means having physical properties that are different in different directions. Thus, for effective enhancement of performance, properties must be enhanced in the appropriate direction and this is achieved in the process. There is a change in the stress yield curve with the removal of a clearly defined yield point.

Normally, an increase in strength is not conducive to an increase in both toughness and ductility. Brittle failures originate from defects that act as stress raisers. Although crack development and propagation is hindered by an increase in toughness, crack blunting by localised yielding is an effective part of the overall mechanism. It is the balance between strength and toughness that determines if brittle or ductile properties predominate. The enhanced toughness of biaxial pipe is shown by higher impact resistance and greater resistance to failure by slow crack creep mechanisms. This mechanism is based on the laminated structure of biaxial PVC, where crack propagation is hindered by the reduction in stress concentration at the crack tip as the crack passes through each layer.

7.2.2 Sheet

Biaxially orientated corrugated PVC sheets are produced for outdoor protection against the elements. Impact strength, including low-temperature impact, derived from the orientation process is significantly higher than that of standard extruded PVC corrugated sheet.

7.3 Blends and Alloys

7.3.1 Flexibilisers/Internal Plasticisers

In an attempt to move into application areas requiring the rubbery or elastomeric properties given by thermoplastic elastomers (TPE) and thermoplastic olefins (TPO), the mechanical blending of PVC resins with other elastomers has been developed. This internal plasticisation is the effect produced by structural groups incorporated into a polymer, which also has the effect of lowering T_g. However, cost efficiency and ease of processing have to be considered.

Chlorinated PE (CPE) modifiers have good compatibility with PVC, due to a similar structure, and are suitable for flexible PVC applications where a high degree of flexibility combined with durability and weatherability is required. The chlorine content of the CPE resin for this use is 42% and addition level would be >20 phr. Acting as a permanent plasticiser, the liquid plasticiser component can be eliminated or substantially reduced. End uses are in sheets, pond and reservoir liners, and roofing membranes.

Nitrile rubbers (NBR) are blended into PVC-P formulations giving vinyl-based TPE for use in glazing gaskets, footwear, tubing, and so on. NBR are copolymers of acrylonitrile and butadiene which are compatible with PVC and available in powder form, partitioned with PVC or $CaCO_3$ for ease of mixing and dispersion. Relatively easy to process, although high melt viscosity may be an issue, formulations including NBR have good oil and chemical resistance, better low-temperature flexibility, and improved abrasion resistance. Formulations with low compression set can also be utilised. Plasticiser loss is also reduced because of the affinity of NBR for plasticisers. Weatherability is poor.

ABS is added to semi-rigid PVC-P formulations to improve vacuum formability (hot melt strength and elongation) with increased tear strength and low-temperature flexibility necessary for automotive applications.

Ethylene–vinyl acetate copolymers (EVA) are used as polymeric modifiers. A vinyl acetate content from 45 to 70% confers good compatibility with PVC. The resulting formulations have good low-temperature flexibility and good weathering and ageing properties. High filler acceptance, including additives for flame resistance and low smoke emission, may also give improved performance characteristics.

Ethylene-based terpolymers, including EVA–carbon monoxide and ethylene–butyl acrylate–carbon monoxide, are available in a range of melt indices and molecular weight distributions to replace plasticisers at the higher performance specification end of flexible PVC. They have extremely good compatibility with PVC, with good clarity.

Graft copolymers of EVA copolymer with PVC combine the rubber elasticity and low-temperature characteristics of EVA with the mechanical properties and chemical resistance of PVC. The EVA content is varied, with the high EVA content grade suitable for plasticiser replacement to give flexible materials with very low volatility and migration.

7.3.2 Ultrahigh Molecular Weight (UHMW) PVC

A manufacturer in the USA, Teknor Apex, has introduced PVC elastomer compounds, based on UHMW resins, with a K value ranging from 80 to 100 [10]. Although more costly to produce, due to the lower temperature for polymerisation and to the higher molecular weights the resins are more crystalline with a higher porosity (thus capable of absorbing high plasticiser levels). As a result, the resin provides enhanced physical and elastomeric properties and retains formulation versatility. The physical properties of the compounds, including low-temperature brittleness and abrasion resistance, are superior to standard PVC-P. Compression set characteristics (deformation in a material remaining after it has been subjected to and released from a compressive force, usually expressed as a percentage of the original compression) at room temperature are similar to TPE. Flex fatigue resistance is also good. Super-soft materials with good physical properties and dry surface feel can be produced.

Applications include non-kinking medical tubing, medical resuscitators, gaskets and seals of low compression set and chemical resistance, weather strip, specialised electrical cable sheathing, and so on.

7.4 Nanocomposites

Composites based on layered inorganic compounds, such as clays, have been of interest for a number of years. The sheet-like structure of naturally occurring clay minerals, such as aluminosilicates, has layers with a thickness of around 1 nm; the lateral dimensions of these layers are up to several micrometres. This gives a very high aspect ratio (ratio of length to thickness) of above 1000. This feature has been utilised for incorporation of various materials. Synthetic (and purer) clays are also available. The clays are usually chemically modified to improve compatibility by cation substitution to increase layer spacing and reduce surface energy. This converts the clay surface functionality from hydrophilic to hydrophobic/organophilic. However, the most widely used ions are alkylammonium, which have a negative effect on PVC heat stability.

Common terms used are:

- *Intercalation* meaning incorporation of the required material between the layers.

- *Exfoliation* meaning cleaving off of the surface, exposing fresh surface for separation. This results in delamination and complete and uniform dispersion, therefore maximising the interactions of the components. The entire surface of the layers becomes available for the polymer.

Nanocomposites are nanoclay-based materials that contain the nanometer-sized clay at a low level in the resin system. Operating at a molecular level, these material types can give a large improvement in properties of the composite material, such as operating temperature, flame retardancy, barrier properties, stiffness, and toughness.

The influence of nano-precipitated calcium carbonate has already been covered in Section 3.6.1. To achieve good dispersion, a masterbatch concentrate must first be utilised. It is claimed that partial replacement of impact modifiers can be made using this material.

In comparison to other polymers, there have been relatively few details of investigations into PVC nanocomposites, but interest is increasing.

7.4.1 Melt Intercalation

Melt intercalation is based on blending the molten material with an organoclay to optimise the interaction between the two.

PVC/montmorillonite (MMT) nanocomposites have been prepared by blending organoclays of differing hydrophilicity with PVC and plasticiser. The thermal stability problems attributed to the quaternary amine used in the organoclay were overcome by pre-treating the organoclay with the plasticiser. The degree of clay intercalation was determined and the co-intercalation of the plasticiser facilitated exfoliation. Improved dimensional stability and barrier properties were obtained [11, 12].

The influence of alkyl quaternary ammonium on the heat stability of intercalated PVC/alkyl quaternary ammonium-modified MMT composites, compared to PVC/MMT composites, has also been evaluated [13].

Intercalated and partially exfoliated PVC/clay nanocomposites have been produced by melt blending. The best mechanical properties were achieved at 2% clay loading with 5–10% plasticiser content [14].

The melt blending and preparation of PVC/sodium MMT have been extensively tested as regards structure, thermal properties, dynamic mechanical properties, flammability, and smoke emission [15].

Epoxy resin has been suggested as a compatibiliser for PVC-U/MMT nanocomposites, with improved transparency and processing stability [16]. Transparency improved with increasing MMT content, the clay being pre-treated with the epoxy resin.

The presence of clay has been noted to retard the chain stripping thermal degradation of PVC-P, with enhanced char formation [17].

A study on the effect of different clay treatment on PVC/sodium MMT nanocomposites has shown that the content of organically modified MMT should be kept below 5% by weight to improve mechanical properties and processing stability with optical clarity retention [18].

7.4.2 Solvent Method

Solution blending of PVC with sodium MMT and an organically modified clay, using tetrahydrofuran as solvent, was found to produce a mixed immiscible intercalated nanocomposite with the clay causing a change in the degradation path of the polymer.

The solvent method is obviously more restrictive as it requires solvent removal and reuse for manufacturing on an industrial scale.

7.4.3 In Situ Polymerisation

With this technique, a layered silicate is first swollen by a liquid monomer, with the monomer migrating into the layers so that polymerisation can occur within the intercalated sheets with the clay layers becoming completely exfoliated.

In situ suspension polymerisation of initiator and comonomer-modified MMT in the presence of free radical initiators to give polymer layered silicate nanocomposites has been investigated [19]. Exfoliated nanocomposites were obtained in both cases, although monomer conversion was low using the initiator-modified MMT.

7.5 Wood Composites

The use of wood flour in plastic composites has expanded considerably, particularly in the USA. In comparison with traditional products, wood-filled PVC has superior weathering resistance but can be used as wood. Filler levels of up to 40–60% are typical and the main application is in decking and window components. However, high-density polyethylene-based wood composites have a much larger market share, particularly including recycled HDPE. Polypropylene can also be used as the plastic component. The advantages for the PVC composite are that coupling agents are not required (both wood and PVC are polar materials), weathering resistance is better, and burning behaviour is improved. Service temperature is also higher but the PVC is more brittle.

Processing is carried out on conventional twin-screw extruders with feeding support using crammer feeders. Drying of the wood fibre is necessary at some stage of the process before the polymer melts. The use of pelletised compound for processing on single-screw extruders is also common.

The attraction of this process is the use, or potential use, of waste wood products and recyclable polymer. The wood flour is sourced from sawdust and shavings which can be derived from hard or soft wood and is hammer milled to a very fine powder. Other cellulose sources are also possible, namely flax, rice hulls, jute, and so on.

Significantly decreased thermal linear expansion (in comparison to PVC-U) is a feature of the composites along with improved moisture resistance (in comparison to wood).

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8 Post-processing and Assembly

8.1 Post-processing

8.1.1 Thermoforming

Calendered or extruded sheet can be thermoformed to shape by applying heat, using vacuum or pressure forming over a preform or mould, and cooling.

The vacuum forming process is particularly suitable for polyvinyl chloride (PVC)-based formulations, due to good melt extension and strength properties over the softening temperature range.

This process involves heating a flat sheet using radiant electric heat (heating can be from one side or both sides) to a softened state (above the glass transition temperature, T_g) followed by the deformation of the sheet over the mould and into the shape required. The deformation occurs due to all the air between the sheet and the mould being removed, creating negative air pressure. The mould may need to be maintained in a particular temperature range to allow slip but also to induce forming. Cooling may be by forced air and/or water mist. The resulting product has variable thickness due to the induced non-uniform biaxial stretch. PVC-based materials are relatively easy to thermoform, due to their highly elastic behaviour over a fairly wide temperature range above T_g.

Tooling can be basically of concave shape (female, negative) into which the sheet is drawn or of convex shape (male, positive) over which the sheet is formed. Tools are not subject to high stress and can be made from aluminium or fibre-reinforced epoxy or polyester resin with fine holes or slots through which vacuum is applied.

Small products, e.g., packaging, can be formed using this technique, in high-output machines using multi-cavity tools and roll-fed sheet material. Larger, more complicated products can be fed with pre-cut sheets at a slower rate.

Pressure forming utilising positive pressure (up to 0.3 MPa) in addition to the atmospheric pressure used in vacuum forming can create an appearance similar to injection moulding with close tolerances, sharp detail, and selective undercuts. Cold flow and excessive thinning are reduced. Mechanical plugs may also be applied to assist material into complicated sections.

In comparison to injection moulding, thermoforming offers economical advantages due to low equipment costs and ease of changing mould designs. However, the process is limited in the shapes it can produce, and by the fact that the forming must be capable of being demoulded from the tool.

8.1.2 Printing and Coating

Surface treatments are often necessary for aesthetic and performance reasons.

8.1.2.1 Printing

The ability of plasticised PVC (PVC-P) to be printed in many different designs and styles, from a simple tile effect to a digital photograph image, is at the heart of the popularity of this material for many different end uses.

Printing can involve the use of both solvent- and non-solvent-based inks, which are applied to the surface using rollers, pads, silk screen, and inkjet or laser printers. Waterborne coatings are environmentally more desirable.

Printing on vinyl surfaces can be problematic due to the influence of the formulation ingredients, particularly the plasticiser (if present), heat stabiliser, and lubricants, on print acceptance and adhesion.

For a surface to be easily printed, a high surface energy is necessary to allow wetting. The problem is exacerbated by the increasing use of water- or solids-based inks requiring higher surface energy substrates. PVC itself has a reasonably high surface energy, 41.9 mN/m, but with the inclusion of different additives this can decrease to as low as 26–29 mN/m [1].

Printing with solvent-based inks requires surface energies of ~38 mN/m and with water-based inks requires higher values. PVC-P for printing applications must be formulated to take this into account. For particular cases, a pre-treatment may be necessary to remove surface layers and to modify the substance chemically. This may involve a solvent/primer bath or corona treatment. Corona treatment involves exposing the surface to an electrical discharge which causes oxygen molecules within the discharge area to break into their atomic form and bond to the ends of the molecules in the substrate. This results in a chemically activated surface with a higher surface energy.

For inkjet and laser printing, a special surface coating is applied to optimise ink adhesion and colour reproduction.

Test inks are available, with different surface energies, to test the wettability of films to standards DIN 53364 [2] and ASTM D2578-04a [3].

Chemical embossing of flooring and wall coverings is based on the incorporation of a blowing agent inhibitor (which prevents the decomposition of the blowing agent) into the appropriate print area. This gives the raised tile or stone effect.

8.1.2.2 Surface Coatings

Coatings can be applied both for functional and decorative effects. Unplasticised-PVC (PVC-U) may be painted. Light sanding and a detergent wash will certainly help prior to painting. A primer may also prove beneficial for adhesion. Painting would only be appropriate if a colour change was required, but bearing in mind the good outdoor weatherability of PVC-U, it may detract from the long-term weathering performance of outdoor products.

Painting of new PVC-U items is more difficult due to the low surface energy, and should only be carried out by those experienced in this area. It is easier to paint and achieve good adhesion on weathered material. Water-based coatings, such as acrylic-based latex paints, have been found to preserve the physical properties of the substrate. Solvent-based coatings containing aromatic hydrocarbon solvents

(toluene, naphtha, and so on) should be avoided, due to the negative influence on impact properties. Paints based on vinyl chloride and vinyl acetate, possibly modified with other monomers, are also suitable. In addition, two-part polyurethane (PU) -based paints are also recommended. In most cases, all paint application techniques, such as brush, roller, and spray, can be used.

Over-painting of PVC-P is also possible, e.g., wall covering, using acrylic-based latex paints.

Foil Coating for Windows and Doors

Foil coatings can be laminated in-line onto PVC-U profile used for windows, usually with a wood grain effect or solid colour. Hot melt adhesives can be used. The foil can be an ultraviolet (UV)-resistant acrylic film or a specially formulated semi-rigid PVC-P film.

Different colours and a matt satin effect, with a slight texture, can also be achieved with a coating based on PU and polyamide (Decoroc®).

Acrylic Topcoat for Flooring

UV-cured acrylic clearcoats on top of a PVC-P wearlayer are also used, giving improved weathering performance and scratching and abrasion resistance to flooring applications.

Metallising and Electroplating

Plastic surfaces can be given a metallic appearance using metallising and electroplating techniques. However, PVC is not used in applications where metallising or electroplating is necessary. The use of a metallised polyester film laminated to PVC would be the preferred option.

8.2 Assembly Techniques

Different joining techniques are used to fabricate PVC into finished articles. All welding techniques involve the application or generation of heat to soften the material while pressure is applied simultaneously. Solvent cement jointing relies on softening/swelling of the material. Mechanical fastening is also possible.

8.2.1 Welding

Like all other plastics, PVC can be welded by application of heat and pressure. Plastic welding techniques can be divided into three process groups:

- Those involving mechanical movement known as friction welding, and including spin and vibration welding, which are recommended for joining PVC-U parts together.

- Those involving heating via high-frequency sound energy (ultrasonic welding suitable for PVC-U) or high-frequency alternating current, particularly suitable for PVC-P.

- Involving external heating, such as hot plate and hot gas welding, also suitable for PVC-U. Hot gas welding can also be used for PVC-P.

The choice of the welding technique depends on the area of the joint, and the number and the shape of the parts to be joined. The strength of the welding depends on the geometry of the component welding method and welding parameters. The selection of the welding method and the design of the component should be considered carefully at the design stage.

8.2.1.1 Friction Welding

Friction welding techniques include:

- Spin welding used for assembling round or cylindrically shaped parts, with one component spun against a mating component that is held stationary under applied pressure.

- Vibration welding used to join large or irregularly shaped parts through frictional heat and pressure generated in a linear or orbital vibrating motion. As with spin welding, the surface of one part is vibrated against the other, which is held in a stationary position.

If the correct procedures are used, both techniques give a weld strength that is equal to the tensile strength of the parent material. The heat generated by the friction melts the material at the interface between two and three seconds. Further time is required to align the parts and to hold them together under pressure until a solid bond is formed. The main welding parameters are rotational, linear, or orbital speed, friction pressure, forge pressure, displacement, and duration.

8.2.1.2 Ultrasonic Welding

Ultrasonic welding involves the use of high-frequency sound energy to soften or melt the material at the joint. Pressure is used to hold the parts together with ultrasonic vibrations applied at right angles with a frequency of 20–40 kHz. The vibratory energy is converted to heat through friction. It is a very fast but somewhat expensive technique, due to tooling, and is suited to mass production. It is also used for staking (melting and reforming a thermoplastic stud to give a mechanical lock), spot welding, and film sealing.

8.2.1.3 Radio-frequency Welding

The welding of PVC-P to itself and to PVC-U materials is best achieved using radio-frequency (RF) welding. This is also known as HF (high-frequency) welding. RF welding requires high dielectric properties of the material to achieve the heating by HF alternating current. The technique involves subjecting the parts to a HF electromagnetic field applied between two metal bars. These bars also apply pressure over the heating and cooling time interval, which can vary. The dynamic electric field causes the polar PVC molecules to oscillate, with some of this motion being translated into thermal energy. The resulting bonds can be as strong as the original material.

This technique is typically used for heat sealing of packaging, and so on. RF welding is also used to apply vinyl, compact or foam, appliqué patterns for fashion designs, logos, and advertising to T-shirts.

8.2.1.4 Hot Plate Welding

The manufacture of PVC-U windows utilises a hot plate, pressure welding technique on a mitre-cut profile, using a temperature near 240–250 °C. The process involves a heated plate being clamped between the surfaces being joined, until they soften. The plate is withdrawn and the surfaces brought together under controlled pressure for a specific period of time. After being allowed to cool, removal of the weld flux or spew is carried out by routers. Corner weld strength test data must satisfy the appropriate national standards.

The other variations of hot plate welding are hot tool, socket, butt fusion, and saddle. Techniques used by the gas and water industries to join and repair pipelines include butt fusion, electrofusion socket welding, and socket jointing. Heated element butt fusion starts with planing the cut surface of the pipe, heating in contact with a heated element, and then joining and cooling under pressure. Socket welding is used where a heated pipe is inserted into a heated fitting. Electrofusion fittings are used where socket welding is not possible.

8.2.1.5 Hot Gas Welding

Hot gas welding utilises a stream of hot gas (usually compressed air) generated in a heating coil as it passes through a welding gun. The hot air is directed towards the joint and a PVC filler/welding rod may also be used to form the weld. This is a manual process and the quality of the bond depends on the skills of the operator.

8.2.1.6 Laser Welding

Laser welding techniques are still being developed. Laser welding involves a part absorbing electromagnetic energy and converting it to heat. Conduction welding utilises a carbon dioxide (CO_2) gas laser, with a wavelength of 10.6 μm, which melts both materials in the joint and can also be used for high-speed cutting. Transmission welding only melts material at the joint interfaces and utilises other laser sources such as diodes, based on indium and gallium semiconductors (wavelengths of 808 and 940 nm), and Nd:YAG (neodymium, a rare earth lanthanide element, doped in yttrium aluminium garnet) with a beam wavelength of 1064 nm. Thermoplastics transmit near-infrared (IR) radiation between 600 and 1000 nm.

8.2.2 Adhesion

Bonding techniques involving adhesives are also common and many proprietary systems are available for PVC-U and PVC-P applications for self-adhesion or adhesion to other surfaces. Surfaces must be solvent cleaned prior to adhesive application.

Typical adhesives can be based on vinyl chloride/vinyl acetate polymers, PVC itself, polychloroprene, PU, and acrylonitrile butadiene. Typical solvents used in adhesives for bonding PVC substrates to themselves or other materials are tetrahydrofuran, methyl ethyl ketone, acetone, toluene, and cyclohexanone. Two-component epoxy or polyester systems can be used.

The flexibility of PVC-P film makes it ideal for many industrial tape and label applications. Pressure-sensitive adhesives based on acrylic polymers and containing acrylates, acrylic acid, and vinyl caprolactam have been recommended.

8.3 Mechanical Assembly

8.3.1 Machining, Cutting, and Fastening

PVC-U can be machined easily. High speeds are possible if there is sufficient cooling. Normal safety precautions as regards handling of swarf and dust apply. Sharp carbide-tipped tools and standard drills are suitable.

Fasteners with thread-cutting screws and clips can be used for joining PVC-U to itself. Thread-cutting screws are preferred to thread-forming screws, due to the latter inducing high stress levels caused by displaced material.

Riveting is also possible where a high clamping force is required. A washer should be applied to the plastic side of the assembly to distribute these high forces over a larger surface.

Permanent mechanical assemblies can also be made by the use of heat or welding techniques to deform plastic ribs, pegs, or studs over the second component (staking).

In snap-fit fastening, two parts are joined through an interlocking configuration that may be moulded into the parts. A protrusion on one part is briefly deflected during joining to locate in a depression or undercut moulded into the other part. The force required for joining can vary depending on the part design. Depending on the locking angle, these connections can be either permanent or easily released. The elasticity of PVC-U makes the material suitable for snap-fit joints. These joints are commonly used in the assembly of fencing, siding, guttering, and so on.

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9 Sustainable Development

Polyvinyl chloride (PVC) has been at the centre of a continued environmental campaign against its use and it is unfortunate but timely that all the issues around modern society have been placed first at its door. No other industry has had to face (yet) the searching questions about the need for sustainable development. The PVC industry has had to gear itself up to respond to these campaigns and this is covered in this chapter.

Sustainable development is not only about being able to advance and improve the standard of living today, but ensuring that future generations can also have the same possibilities. Accordingly, the earth's resources and life support systems should not be overloaded or impaired in meeting these objectives. These should be balanced between satisfying environmental, economic, and social needs.

9.1 Environmental Attack and Response

The Greenpeace organisation's attack on PVC is based on its anti-chlorine stance. This is the 'devil's element', in their terms, due to the use of high energy to generate chlorine and the creation of an extremely reactive form that is not widely found in nature and that results in products and wastes that are toxic to human health and the environment. PVC, being an organochlorine derived from vinyl chloride monomer (VCM), has become lumped together with products such as the pesticide dichlorodiphenyltrichloroethane (DDT) and the refrigerant and aerosol gases chlorofluorocarbons (CFC). Both of these products are now considered to be persistent organic pollutants (POP) due to their stability and resistance to natural breakdown processes and are now banned.

Other POP are dioxins, which are by-products of many processes involving chlorine. Dioxins are a group of chemical compounds made up of two chlorinated benzene rings connected by one or two oxygen atoms. There are several hundred in number, but are based on two family types: the chlorinated dibenzo-*p*-dioxins (PCDD) and chlorinated dibenzofurans (PCDF). PCDD and PCDF can be produced as by-products of some manufacturing processes and also naturally. They are also formed as a result of combustion processes such as waste incineration and burning fuels such as wood, coal, and oil. Studies have shown that exposure to certain dioxins at high enough doses may cause a number of adverse health effects. Dioxins are an environmental contaminant as a result of many different manufacturing and combustion processes over many years. The dioxins occurring in the environment are complex mixtures of 210 congeners, most of which are believed to pose no risk to human health. From these 210, 17 are reported to have potential health effects. For this reason, an international system has been developed that assigns toxicities to each congener relative to the most toxic form. A toxic equivalent factor (TEF) has been assigned to each of these 17 dioxin congeners. This weighting factor is multiplied by the known concentration of the congener to give the toxic equivalent (TEQ). The toxicity of any mixture is given by the sum of the TEQ. The TEQ figure takes account of the relative strengths of the dioxins to enable comparison with other results. Dioxin emissions resulting from the PVC cycle have been noted as insignificant in comparison with other sources [1].

In the 1970s the link between exposure of PVC polymerisation industry workers to high concentrations of VCM and their subsequent development of cancer of the liver was established. Various standards were introduced to protect workers by limiting VCM exposure. Current issues now focus on emissions from the polymerisation plant into the surrounding area and during subsequent processing of the polymer. VCM transportation between manufacture and use has also been an issue.

Greenpeace and other environmental organisations also have a campaign against the 'harmful' additives [plasticisers, heat stabilisers, and volatile organic chemicals (VOC)] in relation to 'leaking' (leaching or emission) in use and disposal (incineration or landfill). This is based on concerns regarding the worldwide build-up of synthetic chemicals in the environment and the potential damage for the future. The main issues are chemicals that are persistent, bioaccumulative, and toxic (PBT). Another group of chemicals causing concern are endocrine-disrupting chemicals (EDCL). These EDCL can interfere with the normal functioning of human and wildlife hormone systems, to produce reproductive, developmental, and behavioural problems. In some cases, EDCL can also be persistent and bioaccumulative. Greenpeace also has concerns about the 'PVC waste crisis' in light of the large volume of long-life PVC products due to become waste in the coming decades (based on products first being used in the 1960s). Greenpeace estimates that worldwide approximately 300 million tonnes will start to enter the waste stream by 2005 and have a sceptical view of the realistic capability for the recycling of PVC. This is based on costs for separation and collection, which makes the recyclate price uneconomic in comparison to virgin PVC. They also consider that there is limited potential for recyclate in the current PVC market.

Incineration with energy recovery is, in Greenpeace's opinion, not a sustainable option due to the generation of less energy than was used to make the incinerated material. There are also issues with emissions of CO_2 (greenhouse gas), dioxins, vinyl chloride, lead, and cadmium. Disposal of the resulting solid wastes including the salts generated from hydrochloric acid neutralisation and containing heavy metals would require disposal in landfill as a hazardous waste.

The export of PVC scrap and waste from Europe and the USA to South East Asia, including China and Indonesia, for recycling into so-called lower quality products is also an issue. Recycling in that part of the world is a growing industry due to much lower labour costs and this reflects the supply and demand nature of the global market.

At some points, the actions of the environmental non-governmental organisations (NGO) became very demonstrative and emotional resulting in action at EU level and deselection of PVC in certain areas.

An interesting response was from the Chlorophiles, which is an independent, non-profit organisation of workers from the chlorine and PVC industry in Europe, who wanted to react to the allegations against their work. Formed in 1994, they have led various campaigns and protests against the actions and statements from Greenpeace, both in person and via their website. They have always attempted to present the actual scientific data in response to the emotional arguments from Greenpeace. They also aimed to have an open scientific debate about the various issues, but Greenpeace have never accepted their invitation.

The Chlorophiles have pointed out the relative abundance of bound chlorine in nature, the amount of organochlorines made in nature, the higher dioxin levels found in wooded areas in comparison to industrial environments, and the significant benefits of chlorine use covering medicine manufacture, disinfectants, bleaching, silicon chips, and so on. They have also reminded everyone about the definition of risk covering the product of hazard and exposure. Thus, the risk is the probability or

chance that the hazard will lead to illness or death. Data have been presented showing the low fatal accident rate and risk of death from working in their industry.

For the PVC industry, the environmental attack has resulted in Vinyl 2010, the voluntary commitment of the PVC industry in Europe. This followed the EC 'horizontal study' - five studies covering a comprehensive investigation of all PVC issues relating to waste management, the combined results leading to the adoption of a Green Paper on PVC (*http://europa.eu.int/comm/environment/waste/pvc/en.pdf*) in July 2000 followed by public consultation. Vinyl 2010 was introduced to pre-empt any further legislative action (at the time of writing, an EC communication stating EU policy on PVC is still awaited). This is in addition to directives covering packaging, motor vehicle end-of-life (ELV), waste electrical and electronic equipment (WEEE), restriction of hazardous substances in electrical and electronic equipment (RoHS), and so on.

One approach to sustainability, very much focused on the environmental aspect, has been the use of The Natural Step (TNS) framework which applies a systems model based on scientific principles governing the earth's ecosystem. PVC has been evaluated by this process and five long-term challenges set covering carbon neutrality, closed loop waste management, no build-up of persistent organic compounds, sustainability of all additives with phase out of persistent compounds and those having toxic effects, and the raising of awareness about sustainable development within the industry and participation in its achievement.

9.2 Vinyl 2010/Chlorine Industry Sustainability Commitments

Vinyl 2010 is involved in projects in all of the PVC life cycle and has grouped together PVC resin manufacturers, plastic converters, and producers of stabilisers and plasticisers (**Figure 9.1**). These cover pilot projects, R&D investigations, studies and surveys, and various initiatives. In addition, the European chlor-alkali industry has issued sustainability goals, also for 2010.
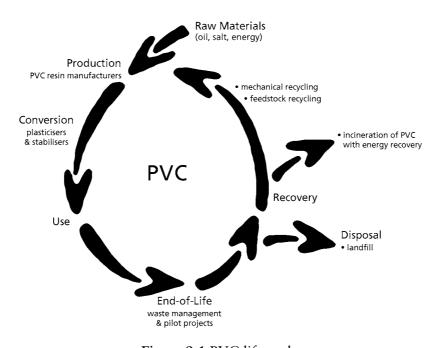
Figure 9.1 PVC life cycle

9.2.1 Chlorine Generation

Euro Chlor (*www.eurochlor.org*), which represents the European chlor-alkali industry, has established a long-term sustainability programme, with goals for 2010. While noting the economic contribution of chlorine and caustic products to economic development, it has agreed the following targets:

- Chlorinated organic chemical emissions – 22 chlorinated substances released to water fell by 98% between 1985 and 2001. A further 75% reduction, based on 2001 baseline (in the region of 0.20 kt), has been set. The release to air, over the same period, was reduced by 90% and a further reduction of 50% has been set for 2010. The target figure is in the region of 2.5 kt per year.

- Mercury emissions – a voluntary target of 1.0 g of mercury emission to water and air, per tonne of mercury cell capacity was set in 1998 to be reached on a national basis by 2007. This has been extended to all the EU 2004 accession country companies. Between 1985 and 2002 there had been a reduction in mercury emission from 8.1 to 1.05 g per tonne of mercury cell capacity.

- Include environmental, social, and economic aspects in all strategic business decisions. This includes mercury cell replacement by membrane technology and non-asbestos separators for diaphragm technology by 2020. There are also targets for reduction in loss time injuries for employees and contractors (85 and 90%, respectively) by 2010. In the same time period, there is a target for a 75% reduction in process incidents and losses and to keep transport incidents at zero.

- Optimise energy efficiency in production by reducing energy consumption by 5%.

- Reduce water usage through recycling.

- Use more hydrogen generated by the industry as a raw material or fuel with 95% being utilised.

- Give high priority to the safe transportation of chlorine. Currently, <10% of all chlorine that is produced in Europe is transported primarily by rail and none by sea.

9.2.2 PVC Production Industry Charters

Resin producers have been working towards minimising environmental impact through full compliance by all of their plants in Europe (*www.pvc.org*).

9.2.2.1 First Charter on S-PVC and VCM Production

European Council of Vinyl Manufacturers (ECVM) member companies agreed an industry charter in 1995 to adopt best available technology (BAT) to minimise emissions to the environment. This covers 12 different environmental standards relating to the suspension polymerised-PVC (S-PVC) resin manufacturing cycle, for compliance by the end of 1998. The conversion of PVC resin to the finished article is not included.

Thirty-eight production sites in Western Europe are involved and the standards are:

- Ethylene dichloride (EDCL) and VCM production
  - Releases to air (per Nm^3)
  - VCM: <5 mg

- EDCL: <5 mg
- HCl: <30 mg
- Ethylene: <150 mg
- Dioxins: <0.1 ng TEQ
- Releases to water
- EDCL: <5 g/ton of EDCL purification capacity
- Copper: <1 g/ton of oxychlorination capacity
- Dioxins: <1 µg TEQ/ton of oxychlorination capacity

- S-PVC production
  - Release to air
  - VCM: <100 g/ton of PVC
  - Release to water
  - VCM: <1 g/m^3 of effluent
  - Concentration in final product
  - VCM: <5 g/ton of PVC for general purpose use; <1 g/ton of PVC for food and medical use.

The first external audit was in 1999 and the second in 2002. As at 2002, the external auditors indicated an improvement from 1999 to 93% full compliance, 4% partial or unconfirmed compliance, and 3% non-compliance. The auditors also recommended reviews to ensure fair comparison across sites, more transparency on reporting incidents and events, and the reduction of the HCl criterion to 10 mg/m^3 to bring it in line with the EU hazardous waste incineration directive (94/67/EC).

Since the last audit, additional information indicates that the goal of full compliance is even closer. Work also continues on improved measurement of emissions.

9.2.2.2 Second Charter on E-PVC Production

The second ECVM industry charter, covering environmental standards for PVC production by the emulsion process, was established in 1998 for compliance by the end of 2003. Auditing took place in 2004.

The standards for emulsion-PVC (E-PVC) production are:

- Release to air. VCM: <1000 g/ton of PVC

- Release to water (for stand alone E-PVC plant). VCM: <1 g/m^3 of effluent and <10 g/ton of E-PVC

- Release to water (where common treatment with S-PVC plant). VCM: <1 g/m^3 of effluent or <5 g/ton of E-PVC + S-PVC

- Concentration in final product. VCM: <1 g/ton of PVC

The audit report, issued in April 2005 [2], showed 71% compliance against the combined three criteria for VCM emissions to air, to water and in the final product. In detail, the VCM emissions to air showed 86% compliance with VCM in aqueous effluents at 71%.

However, 57% of plants achieved full compliance for residual VCM in the final product. Taking account of the amount of final E-PVC produced, 95% complied with the <1 g / tonne. All plants complied with the ECVM BAT of <5 g / tonne as applied in the S-PVC Charter for non-food or non-medical applications. The auditors recommended that either the BAT guidance or the E-PVC Charter be changed to ensure consistency. Improvement plans for some non-compliant companies have already been agreed.

9.2.2.3 Reaction Inhibitors.

Bisphenol A (BPA) has been used as an inhibitor in the polymerisation stage of PVC production for some time. However, EU studies have indicated that emissions to waste water from PVC plants could, under certain conditions, result in concentrations that would exceed predicted no-effect concentrations (PNEC) derived from ecotoxicological studies. Consequently, ECVM member companies agreed to stop using it from the beginning of 2002 and this has been accepted at EU level as a valid risk reduction strategy. A future revision of the ECVM Charter will include a commitment about BPA phase-out to ensure proper compliance monitoring. The other uses of BPA in PVC additives do not present a risk of exceeding current PNEC values (see Section 1.9.3).

9.2.3 Conversion with Additives

Several aspects must be taken into account while considering the impact of PVC additives on human health, safety, and the environment. In addition to pertinent regulations and directives covering worker safety, plant emissions, and specific end uses (water, food, toys, and medical applications), the EU Dangerous Substances Directive (67/548/EEC, consolidated version 92/32/EEC) prescribes how substances classified as dangerous have to be classified and labelled. Provision of safety data sheets is also mandatory.

More recently, the Precautionary Principle has been applied when assessing the risks from potentially hazardous chemicals. This is linked to risk management and is based on the concept of erring on the side of caution when scientific evidence of harm is contradictory or does not exist.

The EU Existing Substances Directive (93/793/EEC) was established for the evaluation and control of the risks of 'existing' substances. Existing substances are chemicals listed in the European Inventory of Existing Commercial Chemical Substances, in use within the EC before September 1981, if produced or imported in volumes above 10 tonnes per year. A systematic framework, for the evaluation of the risks to human health and the environment has been established, based on data collection, priority setting, risk assessment, and risk reduction. This means that substances that are found to be an unacceptable risk within a certain margin of safety are liable to be phased out or their use limited or restricted to certain applications.

In Europe, the EC has adopted a White Paper setting out a new chemical strategy to ensure a high level of protection for human health and the environment and to stimulate innovation and competitiveness in the chemical industry. The Registration, Evaluation and Authorisation of Chemicals system (REACH) will cover existing legislation, including dangerous substances classification and existing substances evaluation and control. Under these proposals, industry will be responsible for testing and risk assessment of its products on a volume priority basis (starting with 1000 tonnes per year but will apply eventually to greater than 1 tonne per year). Authorisation of substances that are carcinogenic, mutagenic, or toxic to reproduction (CMR), and POP will be required. Substances

that are PBT and very persistent and very bioaccumulative (VPVB) will also be identified through further research with a decision about their future use being taken at a later stage. There is also an intention to increase transparency and information about chemicals. Increased responsibility will also pass to formulators and downstream users, who will have to supply data on the particular uses they make of a substance.

Polymers will not require registration provided that their monomers, from which they are derived, are registered. Thus, VCM will require registration, but not PVC.

The impetus for the legislation is the general lack of knowledge about properties and uses of existing substances and a slow and resource-intensive risk assessment process. The chemical industry is in intensive discussions with the EC regarding cost benefits and priorities. A joint exercise has started to test the administrative workability of the system.

Several international regulatory bodies also manage programmes about specific classes of chemical substances. These are the United Nations Environmental Program (UNEP), the Organisation for Economic Cooperation and Development (OECD), and the Oslo Paris Commission (OSPAR).

9.2.3.1 Phthalate Plasticisers

The European Council for Plasticisers and Intermediates (ECPI) producers have committed to carry out research, undertake risk assessments, support the concept of lifecycle inventories and make available the relevant information. In 2004 €630k was contributed to build up a scientific database covering different health and environmental issues.

9.2.3.1.1 Phthalate Risk Assessments

The final summary and full EU risk assessment reports have been published by the EC's European Chemical Bureau (ECB). These final reports require endorsement by the EU Member States Article 15 Committee, before publication in the EU's official journal. The risk assessments were carried out in accordance with the Existing Substances Directive.

These reports have shown no risk to humans or to the environment for diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). Prior to these results, some PVC processors had already begun to change from di-2-ethylhexyl phthalate (DEHP) to DINP or DIDP in PVC formulation (DEHP decreased in 2003 to 24% of the total of phthalates used from 42% in 1999).

The risk assessment for DEHP is scheduled for completion in June 2005. So far the data shows that exposure of the general population is well below levels (at least 280 times) at which health might be put at risk. Therefore no risk reduction measures are needed for the general population. The areas where risk reduction may be necessary are:

• Use in children's toys (but DEHP is not used in toys intended to be put in the mouth).

• Possible exposure to workers in factories (only where adequate precautions are not already being taken).

• Some localised environmental exposure near to factories (and should be managed closely by strict emission controls).

- Use in specific medical areas covering adults undergoing long term haemodialysis, neonates undergoing transfusions and children undergoing long term blood transfusions. This is in conflict with the relevant EU Scientific Committee which has already stated that it can make no recommendations to limit its EU hazard classification labelling (which factors into the risk assessment) has categorised DEHP as toxic to reproduction.

The risk assessment for dibutyl phthalate (DBP) shows some potential risks to plants in the vicinity of processing sites and possibly to workers through inhalation. This will require the implementation of straightforward measures wherever they do not already exist. Hazard classification labelling has given DBP a dangerous for the environment and toxic to reproduction categorisation. DIBP is an alternative for DBP and does not have the toxic to reproduction hazard classification.

The risk assessment for butylbenzyl phthalate (BBP) is still awaited, as scientific data is being considered. The current status is that no risks to human health or the environment have been identified.

Under EU hazard classification and labelling directives, BBP has been classified as dangerous for the environment and toxic to reproduction.

9.2.3.2 Adipate Plasticisers

PVC food packaging film (cling film) has been used for a number of years for wrapping fresh meat, for food storage, and for protecting food in the home.

The most common plasticiser used in this application is di-2-ethylhexyl adipate (DEHA), in combination with polymeric adipate plasticisers and epoxidised soya bean oil (ESBO). DEHA is used in preference to phthalates due to improved flexibility at lower temperatures and also gives the necessary permeability to oxygen and water vapour to preserve the freshness of the food.

PVC cling film formulations comply with permitted migration limits, set at levels that are considered totally safe by various health and government organisations (see Section 4.9.1.1). However, some consumer organisations have raised concerns and polyethylene (PE) has been introduced as an alternative stretch film material. A recent Italian university research laboratory study, comparing PVC and PE cling film, has shown that total and specific migration coefficients to fatty foods, for the PVC, were well below the legal limit. The cling aspects were better with resulting superior protection against bacteria [3].

9.2.3.3 Medium Chain Chlorinated Paraffins (MCCP) Risk Assessment/Hazard Classification

Discussions are under way to classify and label 2-(2-Methyl-4-chlorophenoxy)propionic acid (an example of an MCCP) as dangerous to the environment, primarily as regards aquatic effects. For human health, there are also discussions concerning classification for fertility effect issues.

Under the EU existing substances legislation, the risk assessment (environment only) for MCCP is ongoing. In addition to their use as secondary plasticisers for PVC, MCCP are also used as flame retardants for other plastic and rubber products, in sealants, paints, metal cutting and metalworking fluids, leather fat liquors, and so on. Issues are persistence and possible bioaccumulation and some risk reduction measures, for some uses, are anticipated.

9.2.3.4 Heat Stabilisers

The European Stabiliser Producers Association (ESPA) has committed to various initiatives as part of Vinyl 2010:

- Produce yearly statistics on stabiliser consumption by converters and their areas of application covering formulated lead stabilisers, solid and liquid stabilisers containing cadmium, formulated mixed metal solid stabilisers (e.g., calcium zinc primarily based as lead replacement), organotin stabilisers, and liquid mixed metal systems based on barium zinc or calcium zinc.

- Cease sale and use of all cadmium-containing stabilisers since March 2001 in EU member countries. The European Plastics Converters (EuPC) has also agreed not to use these materials. However, it has been recognised that there is a need to ensure that the recycling of cadmium-containing PVC waste will be permitted.

- To compile the necessary data for a full EU risk assessment on lead stabilisers, on a voluntary basis, together with the rest of the lead industry for submission in 2004. The work is compiled by independent consultants and is reviewed step by step by the Dutch authorities, who are acting on behalf of the EU for this assessment.

- The development of alternative stabiliser systems to lead, in a joint commitment with European processors, to replace formulated lead stabilisers by 15% by 2005, 50% by 2010, and 100% by 2015. This is to be measured on the basis of production levels in 2000 (129 kt). However, the first reduction target was achieved in 2004, showing a decrease of 16.7% to 106 kt. The replacement solid mixed metal stabilisers based on calcium zinc or calcium organic increased by 100% in the same period from 17 to 35 kt.

9.2.3.4.1 Cadmium Risk Assessment

Although there are no longer any sales of cadmium based stabilisers in the EU, a risk assessment continues within the EU Existing Chemicals Programme for an update and potential risk reduction measures. A revision is pending on the Restrictions on the Marketing and Use Directive 76/769, which banned all uses of cadmium stabilisers, to include an authorisation to recycle material containing cadmium in building applications.

9.2.3.4.2 Voluntary Lead Risk Assessment

Publication has been delayed, but preliminary conclusions [2] indicate that:

- For workers in the PVC processing industry, there is a need for more information and/or testing.

- For use in PVC and for stabiliser production regarding environmental impact, no further information or testing is necessary and no need for risk reduction measures beyond those which are being applied already.

- For worker exposure in stabiliser production, there is a need for limiting the risks and risk reduction measures, which are already being applied, shall be taken into account.

9.2.3.4.3 Zinc Risk Assessment

Zinc stearate is included, with other zinc compounds, for human health risk assessment under existing substances legislation. Conclusions are that there are no reasons for concern for adverse health effects on workers or consumers due to exposure. Risk reduction measures already being applied are adequate.

9.2.3.4.4 Organotin Risk Assessment

The toxicity of tin compounds to human health and the environment is strongly dependent on the chemical composition. The mono- and di-organotin stabiliser compounds, covered in Section 3.1.2.1, have been tested extensively for human health aspects and environmental issues (*www.ortepa.org/ stabilizers*) with no causes for concern.

Unfortunately, the toxicity of mono- and di-alkyl tin compounds is sometimes confused with the toxicity of trialkyl tin compounds to aquatic life. The primary use of tributyl tin compounds is as biocidal additives in marine anti-fouling coatings and not as stabilisers. These have now been banned in Europe.

A targeted risk assessment on the non-food aspects of the risk to health and the environment posed by the use of organostannic compounds (excluding tributyl tin biocide) is under way. Exposure assessments with regard to food contact applications are also being carried out by the European Food Safety Authority (EFSA). Classification and hazard labelling of organotin stabilisers is not an issue.

9.2.3.4.5 Epoxidised Soya Bean Oil (ESBO)

The use of ESBO in food contact materials is under review in relation to its use in sealing gaskets for baby foods packed in glass jars and bottles. Within the EFSA, the Panel on Food Additives, Flavourings, Processing Aids, and Materials in contact with Food (AFC) has been asked to give an opinion on the risk for infants. In addition, an opinion on the risk for the consumer in general as regards the ESBO derivatives (chlorohydrins formed by reaction with PVC) is requested. Although ESBO is neither carcinogenic nor genotoxic, the estimated exposure to ESBO migrating into baby foods can sometimes exceed the tolerable daily intake (TDI) and the AFC has recommended that a specific migration limit be developed. Further analytical and toxicological data on ESBO derivatives are also required.

9.2.3.5 Antimony Trioxide Risk Assessment

Under the EU existing substances legislation, the flame retardant antimony trioxide is undergoing human health and environment risk assessments. Discussions are ongoing at the time of writing (March 2005).

Classification and labelling indicates limited evidence of a carcinogenic effect with no ecotoxic categories.

9.3 End of Life and Waste Management

The integrated approach to promote resource efficiency within the European plastics industry (Plastics Europe, *www.plasticseurope.org* and *www.apme.org*) focuses on the concepts of prevention (via

reduction at source), reuse, recycling, energy recovery, and landfill (for non-recoverable products and residual waste from recovery operations).

Vinyl 2010 members (ECVM, ECPI, ESPA, and EuPC) contributed in the region of €4.4 million in both 2002 and 2003 to waste management projects. A further €4.1 million was contributed in 2004.

The Vinyl 2010 target is to have an additional 200,000 tonnes of post-consumer PVC recycling by 2010 in Europe (based on pre-enlargement EU: 15 countries and Switzerland). For 2004, the audited tonnage was in the region of 18000 tonnes, a ~30% increase over 2003 [2].

9.3.1 PVC-rich Waste: Mechanical Recycling

Mechanical recycling has to make economic sense and relies on sufficient quantities of homogeneous, separated, and sorted waste. The quality of recovered material should allow production of similar products.

One PVC resin and compound supplier (*www.evc-int.com*) has announced a project to find and evaluate new applications using post-consumer PVC waste. Another supplier (*www.hydropolymers.com*) expects to produce around 5,000 tonnes of recycled PVC during 2004, primarily for building type products.

9.3.1.1 General

In the UK, a government-funded research project (Waste Resources Action Programme; WRAP) was set up (completed March 2004) to establish the viability of recycling facilities to produce higher value products from post-consumer and post-industrial use PVC-rich waste streams. The project involved many industrial collaborators and the research work included market research, practical trials, laboratory testing of recyclates, economic evaluations, and environmental impact comparisons.

The project concluded that around 45,000 tonnes per year of post-industrial PVC-rich waste (mainly off-cuts) is already being recycled to high-grade applications. Some 10,000 tonnes, of post-use waste, is also recycled. Up to 170,000 tonnes per year of post-consumer use PVC-rich waste could be collectable from the UK construction area by 2010. This waste would comprise mainly windows, pipes, and flooring. Other sources of post-use PVC-rich waste (coated textiles, wallpaper, packaging, cable insulation, ELV, and so on) are either too difficult to collect economically or are already exported together with other materials (e.g., copper wire in cables). Several compression moulders have been identified that are able to take substantial volumes of lower grade recyclate to make long-life products which can be substituted for concrete and other materials.

It was demonstrated that high-grade recyclates can be produced from these post-use construction wastes derived from the Vinyloop process or by mechanical separation. Melt filtration could also be a possibility for handling post-use flooring. However, issues of colour (darker), surface defects (particularly relevant for windows), and cadmium content (restricting use to windows, drainage pipes, and so on, as certain PVC applications where there may be regular human contact, e.g., flooring, are not permitted to have more than 100 ppm of cadmium in the EU) have to be considered.

Due to commercial considerations, such as low collection volumes (so high risk of setting up new plants) and low recyclate prices (users reluctant to substitute virgin material), there have been no high-grade

recycling projects in the UK. However, a PVC industry group (British Plastics Federation, BPF) has established a new waste collection pilot scheme with the aim of establishing a clearing house, which contracts the large-scale collection and reprocessing of post-use waste with existing waste collection and recycling companies. In addition, the major PVC compound users commit to buying recyclate at prices close to virgin compound and to use it to substitute virgin material in their products.

An environmental impact comparison has concluded that landfill disposal has the greatest environmental impact. Mechanical recycling (either mechanical separation or the Vinyloop process) has the lowest. This is due to the capability of high-grade recyclate substituting virgin material in new products. Feedstock recycling comes between landfill and mechanical in terms of environmental impact.

In another eco-efficiency study, various treatment options for mixed cable waste have been investigated. This showed that feedstock recycling and a modern municipal solid waste incineration, with energy and HCl recovery, were preferable to landfill. It showed, however, that the selection of a recovery technology must take into account specific national or local conditions. This is due to differences applied in environmental policies.

9.3.1.2 Collection and Separation/Washing/Grinding/Pulverisation

An important feature of processing plastic waste is the collection, dispatch, cleaning, and grinding down to an appropriate particle size to suit the next processing stage. European Plastics Recyclers (EuPR) conducted a study on PVC mechanical recyclers in the EU. The study showed that this is a core business for no more than 30 companies that have the expertise and willingness required to deal with post-consumer PVC waste. To assist a steady supply of secondary raw materials to these recyclers (and so justify investment in additional capacity), a consortium called Recovinyl SA has been set up based on the recyclers and other interested parties. This will facilitate the collection, dispatching, and recycling of post-consumer PVC waste across Europe.

9.3.1.3 Profile

The target in Europe of the European Profile Producers Association (EPPA, the EuPC sector group for windows and related profiles) for post-consumer PVC window waste is also to recycle mechanically at least 50% of the collectable available quantity by 2005. The 2003 target of 25% was exceeded in this area (~4800 tonnes against the target of ~3400 tonnes). Joint collection of post-consumer PVC construction products started in 2003 in the key countries of Germany and the UK, augmenting the collection networks in France and Denmark. Collection and recycling schemes are being developed for Austria, the Netherlands, Italy, Belgium, and Ireland. Another unforeseen factor, which has to be taken into account, is the re-use of PVC window frames and the export of material for recycling elsewhere.

In Germany, despite a market decrease in window units by around 50% in comparison with 1995, there was an increase in collected and recycled waste volumes by over 15%. Joint collection initiatives with the other PVC recycling groups in the construction area were set up and expanded. A major German producer set up a facility for recycling all components from window frames and this has been operational for some time under Veka Umwelttechnik ownership. The FREI (window recycling iniative) recycling scheme has been combined with the Veka system into Rewindo GmbH which is now a consortium of German profile producers utilising this facility. A study has shown that over 11% of dismantled post-consumer windows are being reused and approximately 4,000 tonnes was recycled in 2004 (*www.rewindo.de*).

In France, the network of collection points has been enlarged with a drastic increase in collected volume. However, there is a lack of local capacity for recycling which negatively influences collection costs and this is being addressed.

In the UK, the WRAP PVC project has shown that on the basis of practical trials, 40% post-use window recyclate can be added to produce new extrusions for use in window applications without significant colour or surface defect problems. The BPF is leading a synergistic project (funded by Vinyl 2010 through the EPPA) aimed at finding the most appropriate 'best practice' solutions to collect and manage PVC construction and demolition waste. This will be based on expertise already gained in local authority refurbishment projects and will expand to many more sites. WRAP has investigated the need to increase glass recycling from windows. In its second phase, BPF members will look at unplasticised-PVC (PVC-U) frames.

In Denmark, joint collection efforts with PVC pipe producers now cover more than 75% of the country's municipal waste centres (*www.wuppi.dk*).

Fence posts based on a core of recycled PVC, enclosed in a virgin cap skin, have been developed. At present, this depends on post-industrial waste such as off-cuts and off-specification profile materials as the source.

9.3.1.4 Pipes and Fittings

The target for pipes and fittings (represented by TEPPFA, the EuPC pipes and fittings sector association) is to recycle at least 50% of the available, collectable quantity at end of life by 2005. Despite sluggish economic activity, an interim target of 25% (~6,100 tonnes) for 2003 has been achieved by concentrating efforts on the higher volume waste countries and developing closer cooperation with other PVC-U recycling groups in the construction area.

Denmark has the most successful programme, based on municipal waste centres.

The main focus is the improvement of the financial viability of the collection and recycling schemes in the different European countries. Recovinyl SA will facilitate this process. However, there is now an element of uncertainty on the waste available, due to the higher than expected life expectancy (40 years was used in the original calculations).

9.3.1.5 Wire and Cable

In this application the desire to recycle the copper from wire and cable has always been a driver. Solvent-based technology (see next) is considered to be the best option for reclaiming the PVC component in this area.

9.3.1.6 Vinyloop® Process

This patented process involves the selective dissolution of the PVC compound, separation of non-soluble materials, and precipitation of the pure PVC compound (**Figure 9.2**). This can then be processed into the same application as the original material (see *www.vinyloop.com*).
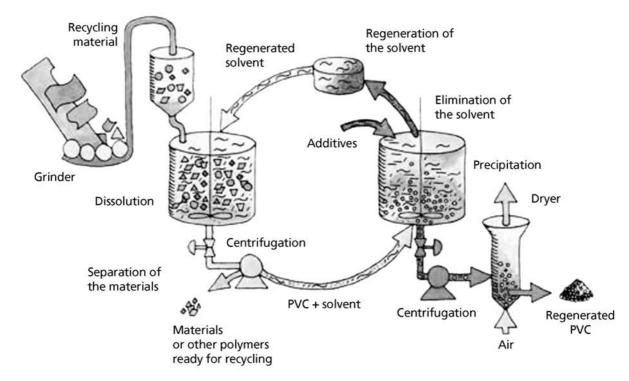
Figure 9.2 Vinyloop process. (Source: www.vinyl2010.org)

The Ferrara, Italy, plant has been operating since 2002 with a 2004 plant target of 7,500-10,000 tonnes. A second plant in Dreux, France, is planned to start up in 2006 with the aim of recycling ~40,000 tonnes of post-industrial and post-consumer waste, consisting of cable, roofing membrane, flooring, windows, etc, has been delayed. However, construction of a new unit, twice as large as the Ferrara plant, will commence in Japan in April 2005.

Based on the Vinyloop technology, Texyloop® has been developed for coated fabrics and involves specific treatment for recycling fibres and compounds (see Section 9.3.1.9).

9.3.1.7 Flooring

The first target in Europe is to recycle at least 25% of the collectable available quantity of PVC flooring waste by 2006, with 50% by 2008. The preferred recycling option is via the Vinyloop process which allows the recyclate to be processed into new flooring products, both calendered and coated.

About 970 tonnes of PVC flooring were recycled or sent for recycling in 2004 (a 68% increase over 2003). In addition to the PVC flooring recycling plant in Germany, there are plans for recycling flooring in the feedstock recycling Stigsnaes RGS-90 project (see Section 9.3.2.2).

Applications for recycled material and cooperation in the collection and future processing of post-consumer waste are ongoing. An extensive R&D programme has shown the feasibility of using the PVC recyclate generated from the Vinyloop process in interlayer applications. Collection schemes are in place in Germany, Austria, and Switzerland with pilot operations being studied or planned in the Netherlands, France, and Belgium.

9.3.1.8 Roofing Membranes

A target of 25% recycling for 2003, aiming for 50% by 2005, has been set for end-of-life, single-ply PVC roofing. This is based on a mechanical cryogenic shredding unit owned and operated by the members of the EuPC sector roofing group and located in Germany. The German market is the largest market by far for this type of roofing and a new collection scheme in partnership with a waste management firm has been set up. The 2003 target was achieved (~540 tonnes followed by ~570 tonnes in 2004), but this process has capacity limitations and was closed at the end of 2004. The solvent-based Vinyloop process has been chosen as a long-term solution with large-scale tests being carried out at the Vinyloop cable recycling facility in Italy. Alternative recycling routes are also currently being considered to augment existing capacity until a new dedicated Vinyloop plant comes on stream in France, planned for 2006 (*www.roofcollect.com*). This could be the production of flooring for areas used by animals.

9.3.1.9 Coated Fabrics

An investigation by EPCOAT (the EuPC sector group for coated fabrics) on collectable waste has indicated that truck tarpaulins and advertising posters could be the highest contributor. Test collection projects have been initiated. Solvent-based recycling is seen as the most promising solution. Alternatively feedstock recycling could be possible.

A study on artificial leather carried out by SFEC (French calendering and coating association) has focused on identifying where and how to collect homogeneous waste. Prefabricators and end-of-life furniture have been identified as the most promising collection targets.

In Germany, an existing waste treatment plant (Friedola) will be renovated and expanded. The technology involves mechanical shredding and compaction of post-consumer waste fabrics for recycling into tarpaulins and artificial leather. A trial collection project, focusing on post-industrial use, has started in a cooperation between IVK (German Plastic Foils Association) and a waste management company. Shredded material is sent to the Friedola plant for recycling or for energy and HCl recovery via incineration (MVR, Hamburg).

In France, the Texyloop process, based on the Vinyloop technology, has been developed to a laboratory pilot unit stage. A larger scale pilot plant is planned for 2004–2005. Longer term, an industrial-scale plant with a capacity of 10,000 tonnes per year is also planned to prepare and treat PVC-coated fabric waste, with an overall investment of €20 million (*www.texyloop.com*). A collection scheme based on 'big bags' has been in existence since late 2002 and the material is stored awaiting start up of this plant. This collection scheme will be extended to other countries (*www.ferrari-textiles.com*).

9.3.1.10 Wall Coverings

A project is underway in the UK at Brunel University looking at recycling possibilities for post-industrial use vinyl wall covering material. The recovery of plasticiser and solvent from waste PVC plastisols generated in the manufacturing process during screen changeovers or end-of-runs, and so on, has been shown to be possible using ceramic membrane separation technology [4].

9.3.1.11 Packaging

Collation trays, as used in supermarkets to transport and display products, remain one possibility for mechanical recycling but this depends on a system to identify the polymer, linked to a suitable

collection system. The polymer type identification, for PVC, has been suggested as '3' with PVC or '3' with V, but there is no mandatory system. Outlets for this material have been identified as a foam layer in co-extruded cladding. PVC water bottle scrap has also been incorporated into the foam core of co-extruded pipe. Another outlet is moulding of rainwater fittings.

However, the separation of PVC from mixed plastic waste, particularly polyethylene terephthalate, is problematical and mechanical recycling is not considered viable.

9.3.1.12 Light Concrete

The recovery and recycling of PVC, and of plastics in general, is often very difficult in building and construction because the polymers are in contact with mortar, cement, plaster, sealing compound, etc. An investigation has been carried out to determine if such PVC waste from buildings can be used for the production of light concrete. Light concrete is used for its low weight and high thermal and sound insulation characteristics in floors and walls. The results were positive with further research necessary.

9.3.1.13 North America Vinyl Recycling

The Vinyl Institute website (*www.vinylinfo.org*) has a specific section covering recycling activities and details of vinyl recycling companies and manufacturers of recycled vinyl products. A study carried out in 1997 showed more than 450,000 tonnes, primarily post-industrial waste, recovered and recycled.

9.3.2 PVC Feedstock Recycling

Feedstock or chemical recycling is seen as complementary to mechanical recycling and seems appropriate for cost-effective treatment of mixed and contaminated plastic waste streams. The concept is that PVC can be broken down into its chemical components which can then be recovered for reuse within a range of industrial processes. With a PVC-rich feedstock, hydrochloric acid is one of the main components recovered. This can then be fed back as a raw material in the PVC production process. Various technologies are being investigated.

9.3.2.1 Combustion in a Rotary Kiln

This process, the Dow/BSL project, depends on combustion in a rotary kiln which delivers recovered chlorine with energy recovery for new VCM/PVC production and is based in a commercial feedstock recycling plant in Germany. The plant is capable of treating high-chlorine-containing waste. A 1,000 tonne trial of mixed PVC waste has been successfully processed and the recovered chlorine used on-site. The mixed waste was primarily flooring and coated fabric, with small amounts of plastisols, cable, and window profile collected via a waste management company as a clearing house. The financial aspects of this process have been evaluated and used to compare cost competitiveness when deciding on larger quantities of PVC waste to be processed using this technology.

9.3.2.2 Hydrolysis and Pyrolysis

This process, the Stigsnaes RGS-90 project, is based on hydrolysis in a commercial hydrolysis plant to dechlorinate PVC waste products to <0.1% by weight of chlorine and subsequent low temperature pyrolysis to post-heat and separate the dechlorinated solid fraction into hydrocarbon, salt and minerals.

The Danish-based plant will have a 50,000 tonne capability and investments are supported by the EU as well as Vinyl 2010. The gate fee for PVC waste processing, including pre-treatment, is quoted at €200 per tonne.

9.3.2.3 Coal Replacement in Blast Furnaces (Redop Process)

The Redop (reduction of ore by plastics) process is based on the dechlorination of mixed plastics from household waste, after separation from municipal solid waste, and co-injection of the waste product together with coal into a blast furnace for steel production. The aim is to replace the pulverised coal (coke) in this process.

Mixed plastics waste streams normally contain 0.5–5% of chlorine by weight, which is much less than PVC-rich waste streams used in other feedstock recycling processes. Mechanical recycling would only yield low-value products, so this promising technology has been followed and supported by various organisations, including Vinyl 2010, in the Netherlands. Bench-scale trials have been very encouraging with the Redop product meeting the steel manufacturers' very demanding specifications. The pellets have a higher calorific value than coal. Further trials on an industrial scale are being planned.

9.3.2.4 New Gasification Processes

Gasification involves conversion of materials having carbon and hydrogen in their chemical structure into clean synthesis gas, syngas, which is a mixture of hydrogen and carbon monoxide. Syngas can be used as an energy source for combustion processes used to generate electricity. The process involves very high temperatures in an oxygen-deficient atmosphere. This destroys the dioxins and prevents the formation of acid gases. The inorganic material is converted to a glassy solid material (slag).

ECVM is continuing to investigate low-cost, robust gasification processes capable of treating contaminated and mixed PVC-rich waste streams. As with all recycling technologies, environmental impact, cost competitiveness, and practical experience have to be assessed. Previous experience in this process was developed on the slag bath gasification technology, developed by Linde.

One PVC and compound supplier (*www.hydropolymers.com*) has established a patented process utilising mixed plastics waste which contains almost 70% of packaging (with 4–10% being PVC). This involves gasification leading to syngas which can be converted to methanol production, with further conversion to olefins. The olefins could be used for VCM manufacture or polyolefins.

9.3.3 Incineration/Energy Recovery

Incineration with energy recovery ensures that the calorific value of oil used in PVC production is recovered at end of life. Incorporating PVC waste in controlled municipal incinerators reduces the need

for additional fuel. A number of independent studies have shown that adding PVC to an incinerator waste stream in which chlorine is naturally present does not increase the generation of potentially harmful emissions. The main focus is the development of appropriate techniques for handling the solid waste residues including the solid fraction derived from the neutralisation of gaseous effluents.

Different processes involving salt reduction and detoxification of the neutralisation salts are being investigated at the pilot-plant scale.

9.3.4 Controlled Landfill

Whatever the nature of the PVC recovery process, there will always be a small residual fraction of waste that is not recyclable. For this reducing fraction, controlled landfill would seem to be the most practical disposal option.

An EC report from Argus (*http://europa.eu.int/comm/environment/waste/studies/pvc/landfill.htm*) in 2000 evaluated the behaviour of PVC in landfill based on a literature survey and on landfill simulation studies at accelerated speed and temperatures up to 80 °C. This concluded that there were some contributions to the contamination of leachate and gas occurring in landfills containing PVC. However, direct correlation with the quantity of PVC, relative to other materials, was not possible.

Other independent studies have confirmed that the presence of consumer products containing PVC in landfill does not constitute a risk to the environment [5]. Lead stabilisers have also been found to release slowly from the PVC matrix and the overall lead is minimal in relation to other sources of environmental lead [1].

9.4 Life Cycle Assessments

The life cycle assessment (LCA) methodology deals with the complex interaction between a product and the environment. The process systematically describes and assesses all the flows to and from nature in a cradle to grave perspective. There are four aspects to be considered in an LCA:

- The first step is the goal and scope definition where the product(s) or service(s) to be assessed are defined, a functional basis for comparison is chosen, and the required level of detail defined.

- An inventory step describes and quantifies the raw materials used, the associated energy requirements, and emissions/disposals to air, water, and land occurring during the life of the product (life cycle inventory, LCI).

- An impact assessment, which assesses the impacts of emissions, energy use, and raw material depletions. These are grouped and quantified into a limited number of impact categories which may then be weighted for importance (life cycle impact assessment, LCIA).

- The final step is interpretation. The results are reported and the need and opportunities to reduce the environmental impact of the product(s) or service(s) are systematically evaluated.

A series of international standards are now available that define the general framework, principles, and requirements for conducting and reporting LCA studies. These are categorised under the Environmental Management – Life Cycle Assessment heading and are ISO 14040 – Principles and

Framework [6], ISO 14041 – Goal and Scope Definition and Inventory Analysis [7], ISO 14042 – Life Cycle Impact Assessment [8], and ISO 14043 – Life Cycle Interpretation [9].

LCA comparisons should be undertaken at the application level rather than at the material level. A study commissioned by the EC on the LCA of PVC and principal competing materials was completed in July 2004 (*http://europa.eu.int/comm/enterprise/chemicals/sustdev/pvc-final_report_lca.pdf*). This was an overview of publicly available information for a variety of applications in order to assess existing information and to identify information gaps. From the 100 LCA identified for PVC, only 30 made comparisons at the application level and many did not fulfil all the requirements outlined by ISO 14040 [6]. The general conclusions drawn for PVC were (1) related to the need for extraction of oil and rock salt and (2) although various technologies for PVC recycling are available, there is an issue with consumers not accepting recycled products with lower optical or aesthetic quality even if technical quality is similar to that of virgin material. Some specific findings were:

- Windows – no overall winner as none of the materials had an overall advantage for the standard impact categories. Design optimisation is seen as the most promising way of lowering environmental impacts.

- Pipe – the production phase was seen to have the greatest influence but with differing viewpoints on material choice. Some studies showed clear advantages for concrete and fibre cement, others for polymer (PVC and PE). Some reports concluded that the material plays no role, as long as cast iron is not included.

- Flooring – linoleum has comparable or slightly fewer environmental impacts in the production phase, but due to significant information gaps in the competitive materials in the use phase, which was found to be the life cycle stage that could influence overall environmental impact to the greatest extent, the analysis was inconclusive.

- Roofing – polymeric materials have lower environmental impacts but the largest influences are the thermal conductivity and good installation and maintenance of the roofing system.

- Packaging – for non-reusable packaging, PVC and PET have similar impacts in comparison to less favourable heavier alternatives. The conclusions are not clear when reuse is taken into account.

The conclusions are being used to counter discriminations by local authorities, etc., against PVC in green procurement and eco-labelling discussions.

In the USA, a draft report combining LCA with Risk Assessments has been issued by the Leadership in Energy and Environmental Design (LEED) Technical and Scientific Advisory Committee of the US Green Building Council covering PVC related materials (*www.usgbc.org/Docs/LEED_tsac/ USGBC_TSAC_PVC_Draft_Report_12-17-04..pdf*). This concluded that PVC was neither a clear winner nor a loser in their investigations.

9.4.1 Eco-profiles

APME have assembled detailed environmental data on the processes operated by its member companies. This information is available on a website (*www.apme.org*) for registered users and contains generic data that could be used to optimise plastics waste management, compile average

industry data for process improvements, and contains inventory data for downstream users to be able to produce their own LCA of individual products. Eco-profiles are available for VCM, PVC resins, and different conversion products.

ECPI also has an eco-profile of the high-volume commodity phthalate esters DEHP, DINP, and DIDP available on its website (*www.ecpi.org*).

9.5 Social Factors

The industry associations ECVM, ECPI, and ESPA have joined together with the European Mine, Chemical, and Energy Workers Federation (EMCEF) to set up as social dialogue on important issues with regular meetings and consultations. This dialogue covers development of Health and Safety Executive standards, training, and transfer of standards to the EU accession countries and dialogue on European works councils.

The aim of Vinyl 2010 is to obtain a gradual enlargement of the voluntary commitment to the new EU member states, even if there are major issues due to the historical structure of the PVC industry in some countries. As a first step, the PVC producers in these countries have committed to achieving the ECVM production charters by 2007. The process for the phasing out of cadmium and lead stabilisers has been started along with the identification of PVC waste streams and volumes.

An important worldwide initiative, which has been running for several years, is Responsible Care, which is the chemical industry's voluntary programme to raise its safety, health, and environmental (SHE) standards and win greater trust. Safety of employees and contractors is a key feature with transparency and verification of indicators covering fatality rates, lost time injury frequency rate, and occupational illness frequency rate. There is also a commitment to provide sufficient information about their operations and products to stakeholders and neighbours. Product stewardship, which takes ownership for products down the supply chain to their final use and disposal, is also an important commitment. There are also targets and goals to reduce emissions.

Responsible Care, which is being developed into a management system in Europe (*www.cefic.org*), is aimed at helping the chemical industry to gain the trust of the public and to operate safely, profitably, and with due care for future generations. Further information is also available at *www.responsiblecare.org*.

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10 Causes of Failure

Like other plastics, polyvinyl chloride (PVC) is not free from product failure during service. A recent study [1] has shown that the main reasons for failure in plastics, in general are environmental stress cracking, dynamic fatigue, static notch failure, creep-related failure, chemical attack, ultraviolet (UV) attack, heat degradation, and wear/abrasion. These are stated in decreasing order of failure.

Amorphous thermoplastics, such as PVC, are particularly sensitive to environmental stress cracking. The reason for this is probably associated with the open structure that allows high rates of fluid permeation. The influence of hydrogen bonding parameters for 65 fluids on craze and crack initiation has been investigated [2].

Dynamic fatigue, as already explained in Section 4.3.4, is not a strong feature of amorphous plastics and unplasticised-PVC (PVC-U) is particularly sensitive in this area. However, this is well known and allowance is made for this aspect in formulation and design - pressure pipes are an example.

Impact-related failure, in the absence or presence of notches, is probably one of the most common reasons for failure of PVC-U products. This may be due to the use of the incorrect grade/formulation for the service temperature and/or poor product design causing stress concentration effects.

Creep is not so much of an issue with PVC-U, but plasticised PVC (PVC-P) may be subject to creep failure at the areas of jointing.

PVC offers good chemical resistance, as noted in Section 4.11.3, but there should be an awareness of chemicals likely to come into contact with the article and the service temperature.

Discolouration caused by UV light and/or heat degradation is another significant reason for short product life. Again, the reason may be due to incorrect formulation and/or awareness of the operating environment, e.g., weather conditions.

Reversible discoloration effects linked to the photochemical degradation of titanium dioxide-pigmented PVC-U have been shown after a period of storage of the aged material in the dark. This has been attributed to the formation of particular polyenic sequences, with the screening effect of the pigment protecting these polyenes against photo-oxidation, so permitting these polyenes to accumulate in the degraded polymer. Pinking of PVC-U profiles in mild climatic conditions has been observed in service. This has been explained by the formation of polyene sequences not completely photo-oxidatively bleached under conditions of oxygen starvation. Predictive tests have also been suggested to recognise this behaviour.

Dirt retention on both PVC-U and PVC-P products can be an annoying failing for consumers. The problem can be due to loss of surface gloss on outdoor exposure, which can attract and retain dirt. For PVC-P articles there may also be issues with plasticiser leaching to the surface and attracting dirt and/or microbiological attack that discolors the material.

Examples of PVC failing due to premature wear and abrasion are extremely limited and are due to incorrect formulation and/or processing.

Embrittlement of PVC-P materials is caused by plasticiser migrating or evaporating during service. The ultimate outcome is product shrinkage and cracking. The correct plasticiser choice to suit the application is necessary.

Product failure analysis is a complex subject. Although it is comparatively easy to establish the main reason for product failure, several possibilities must be considered when product changes are required to avoid the problem. Formulation, product design, processing parameters, die design, and service conditions are some of these possibilities. Usually a compromise has to be considered to arrive at a satisfactory conclusion.

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Abbreviations and Acronyms

OBPA	10, 10´-Oxybisphenoxyarsine
OIT	2-n-Octylisothiazolin-3-one
DCOIT	4, 5-Dichloro-2-n-octylisothiazolin-3-one
ABS	Acrylonitrile-butadiene-styrene
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
APME	Association of Plastic Manufacturers in Europe
ACDM	Azodicarbonamide
BAT	Best available technology
BPA	Bisphenol A
BPF	British Plastics Federation
BBP	Butyl benzyl phthalate
CMR	Carcinogenic, mutagenic, or toxic to reproduction
CDRH	Centre for Devices and Radiological Health
CMAI	Chemical Market Associates
PCDFC	Chlorinated dibenzofuran(s)
PCDD	Chlorinated dibenzo-p-dioxin(s)
CPE	Chlorinated polyethylene
C-PVC	Chlorinated PVC
CFC	Chlorofluorocarbon(s)
CI	Colour Index
CPP	Committee on Products and Processes for Use in Public Water Supply
CPD	Construction Products Directive
XLPE	Crosslinked PE
DIN	Deutsches Institut für Normung eV
DEHA	Di-2-ethylhexyl adipate
DEHP	Di-2-ethylhexyl phthalate
DOS	Di-2-ethylhexyl sebacate
DBP	Dibutyl phthalate
DDT	Dichlorodiphenyltrichloroethane
DIDA	Diisodecyl adipate
DIDP	Diisodecyl phthalate
DIDS	Diisodecyl sebacate
DINA	Diisononyl adipate

DINP	Diisononyl phthalate
DNP	Dinonyl phthalate
DOA	Dioctyl adipate
DOP	Dioctyl phthalate
DWI	Drinking Water Inspectorate
KIWA	Dutch Water Authority
E-PVC	Emulsion-polymerised PVC
EDC	Endocrine-disrupting chemical(s)
ELV	End-of-life vehicle
ESBO	Epoxidised soya bean oil
EBS	Ethylene bisstearamide
EDCL	Ethylene dichloride
EO	Ethylene oxide
EPDM	Ethylene propylene diene monomer
EVA	Ethylene–vinyl acetate copolymers
EAS	European Acceptance Scheme
ECB	European Chemical Bureau
CEN	European Committee for Standardisation
EC	European Community
ECVM	European Council of Vinyl Manufacturers
EDQM	European Directorate for the Quality of Medicines
EFSA	European Food Safety Authority
EMCEF	European Mine, Chemical, and Energy Workers Federation
EuPR	European Plastics Recyclers
EPPA	European Profile Producers Association
EPCOAT	European PVC Coated Fabrics Sector of EuPC
ESPA	European Stabiliser Producers Association
EU	European Union
FIGRA	Fire growth rate
FR	Flame retardant(s)
FDA	Food and Drug Administration
SFEC	French Calendering and Coated Fabric Trade Association
GC	Gas chromatography
DVGW	German Association of the Gas and Water Trade
T_g	Glass transition temperature
GMO	Glycerol monooleate
GMS	Glycerol monostearate
GMP	Good manufacturing practice
GPP	Green public procurement
HDT	Heat deflection temperature

HF	High frequency
HDPE	High-density PE
HALS	Hindered amine light stabilisers
HCl	Hydrogen chloride
IVK	Industrieverband Kunststoffbahnen (German Plastic Foils Association)
IR	Infra-red
IEC	International Electrotechnical Commission
ISO	International Standards Organisation
JIS	Japanese Standards Association
KTW	Künststoffe und Trinkwasser
LEED	Leadership in Energy and Environmental Design
L/D	Length:diameter ratio
LCA	Life cycle assessment(s)
LCIA	Life cycle impact assessment
LCI	Life cycle inventory
LOI	Limiting oxygen index
LTS	Long-term creep strength
LDPE	Low-density PE
MCCP	Medium chain chlorinated paraffin(s)
MDPE	Medium-density PE
TM	Melting temperature
MABS	Methacrylate-acrylonitrile-butadiene-styrene
MBS	Methacrylate-butadiene-styrene
MRS	Minimum required strength
PVC-O	Molecular oriented PVC
MWD	Molecular weight distribution
MMT	Montmorillonite
NBS	National Bureau of Standards
NSF	National Sanitation Foundation
NBR	Nitrile rubbers
NGO	Non-governmental organisation(s)
MN	Number-average molecular weight
OECD	Organisation for Economic Cooperation and Development
OSPAR	Oslo Paris Commission
AFC	Panel on Food Additives, Flavourings, Processing Aids, and Materials in contact with Food
phr	Parts per hundred resin
POP	Persistent organic pollutant(s)
PBT	Persistent, bioaccumulative and toxic
PVC-P	Plasticised PVC
PA	Polyamide

PC	Polycarbonate
PET	Polyethylene terephthalate
PE	Polyethylene(s)
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PNEC	Predicted no-effect concentrations
QA	Quality assurance
RF	Radio frequency
R&D	Research and Development
RoHS	Restriction of hazardous substances in electrical and electronic equipment
rpm	Revolutions per minute
SHE	Safety, health, and environmental
SBI	Single burning item test
SMOGRA	Smoke growth rate
SS	Smoke suppressant(s)
SML	Specific migration limit(s)
SDR	Standard dimensional ratio (ratio between outside diameter and wall thickness)
S-PVC	Suspension-polymerised PVC
ECPI	The European Council for Plasticisers and Intermediates
TEPPFA	The European Plastic Pipes and Fittings Association
EuPC	The European Plastics Converters
TNS	The Natural Step
REACH	The Registration, Evaluation and Authorisation of Chemicals system
TPE	Thermoplastic elastomer(s)
TPO	Thermoplastic olefins
TDI	Tolerable daily intake
THR	Total Heat Release
TEQ	Toxic equivalent(s)
TEF	Toxic equivalent factor
TMA	Trimellitic anhydride
TMPTA	Trimethylolpropane triacrylate
TMPTMA	Trimethylolpropane trimethacrylate
TOTM	Trioctyl trimellitate
TEHTM	Tris-2-ethylhexyl trimellitate
UHMW	Ultrahigh molecular weight
UV	Ultraviolet
UL	Underwriters' Laboratories

UNEP	United Nations Environmental Program
PVC-U	Unplasticised PVC
EPA	US Environmental Protection Agency
VPVB	Very persistent and very bioaccumulative
VCM	Vinyl chloride monomer
VOC	Volatile organic chemical(s)
WEEE	Waste electrical and electronic equipment
WRAP	Waste Resources Action Programme
MW	Weight-average molecular weight
WHO	World Health Organisation
WWF	World Wildlife Fund

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PVC

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