2
Plastic materials: polyvinyl chloride (PVC)

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Abstract: PVC is a ‘contested’ versatile material used in the construction industry. There is always a controversy about whether or not there are significant health risks associated with its use, because a number of toxic additives are involved, and hence there remains the question of whether the health risks of the use of PVC outweigh its many benefits. In the text, the applications of PVC in construction are reviewed and health concerns are briefly summarized. A brief discussion of the replacement possibilities is presented.

Key words: PVC, VCM, plasticizers, additives, safety.

2.1 Introduction

Polyvinyl chloride (PVC), or vinyl for short, or using the IUPAC name ‘chloroethane’ or ‘poly(chloroethanediyl)’, with 57% of mass by chlorine, is an ‘infrastructure thermoplastic’ material. PVC is one of the most important plastic materials used worldwide in various phases of the construction industry, such as pipes, fittings and gutters, window profiles and doors, ceiling tiles, various furniture and upholstery applications, coatings for electrical cables, etc., mainly because of its economy, in addition to its durability and ease of assembly. PVC is also a much used ‘commodity plastic’ in our everyday life, e.g. in clothing, synthetic leather, car seat covers, inflatable structures, etc. PVC with its predicted annual production of around 40 million tons (Ebner, 2009) is second only to polyethylene (PE), the number one commodity plastic. The global market for PVC is expected to continue to grow at about 3–5% per year, with the strongest demand predicted to be in Asia, e.g., China and India, and the EU representing about a fifth of the world market.

2.2 Polyvinyl chloride (PVC – CAS number: 9002-86-2)

PVC is a ‘contested’ versatile material, that is, there is a controversy about whether or not there are significant risks to human health associated with its use. Over its life cycle, a number of by-products and additives, most of which are known to be human toxicants, are involved with PVC materials and hence there remains the question of whether the health risks of PVC use outweigh its many benefits. Controversy extends to both research findings and their interpretation, as well as to the regulatory policy. Green certifying boards have already been asked to award credit for buildings that reduce or eliminate PVC use. Government regulations for the use of PVC in the US and EU have been focused mostly on medical and consumer products, but not on building materials. While this review certainly will not intend to resolve these controversies, it is intended to outline the science relevant to understanding them for the use of PVC as a building material.

2.2.1 Production, structure and properties of PVC

PVC, with chemical formula C_2H_3Cl, is a vinyl polymer composed of repeating vinyl groups (ethenyls), having one hydrogen atom replaced by chlorine on alternate carbon atoms per repeat unit:

$$-[CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}H]-$$

PVC production and processing consists of five major steps (Titow, 1984):

1. Ethylene (C_2H_4) and chlorine gas production
2. Vinyl chloride monomer (VCM) production
3. Polymerization of VCM into polymer
4. Formulation of polymer product with additives
5. Direct molding or end product processing.

VCM is polymerized into the polymer product by an exothermic free-radical reaction at 40–70°C in the liquid state under pressure (in batch reactors) with continual mixing of the 'suspension' to obtain a uniform particle size. After degassing, stripping, centrifuging and drying of the resulting slurry, it is sieved to obtain the powdered 'suspension PVC' product with sizes of 120–150 μm. There are other production methods for PVC as well, e.g. the 'emulsion' technique, which produces smaller sizes (e.g., 10 μm). Suspension and emulsion type PVCs have somewhat different properties and are used for different applications, suspension being the more commonly used. Normally, any PVC product is expected to have less than 1 ppm (parts per million) of monomer (VCM) content left unreacted:

$$\begin{array}{ccccc} H & H & & H & H \\ | & | & & | & | \\ C & = C & \rightarrow & C - & C \\ | & | & & | & | \\ H & H & & H & Cl \end{array} \qquad [2.1]$$

PVC is a white, amorphous, odorless powder, which is stable under normal temperatures and pressures up to 70–80°C, after which it begins to decompose with evolution of hydrochloric acid (HCl) gas and discoloration (yellowing).

PVC was first made in 1872 by the German chemist Eugen Baumann, who did not apply for any patent. In 1912, the German chemist Fritz Klatte working for Greisheim-Electron, Germany, decided to try to react acetylene with HCl (which apparently produced the monomer VCM), and he left the product on the shelf, where it apparently polymerized over time by sunlight. Hence Klatte was the first inventor to receive a patent for PVC (in 1913), using mercuric chloride as a catalyst; this patent expired in 1925. This original method was widely used during the 1930s and 1940s, but has since been superseded by more economical advanced processes, at least in the Western hemisphere.

The importance of PVC and its use was not realized until 1926 when Waldo Semon, an American chemist working at B.F. Goodrich, invented PVC independently. Semon quickly understood that this new material would have a big potential to produce brand-new objects, and he first produced a shower curtain.Semon and B.F. Goodrich immediately patented PVC for the USA (Semon, 1926a, 1926b). Later, Semon tried to produce golf balls and shoe heels from PVC. A great many new uses for this wonderful waterproof material then followed, and PVC was a real success in the world.

Being a thermoplastic, PVC softens if heated and hardens as it cools; and it can be processed by the use of any conventional plastics processing techniques, such as extrusion (specifically for complex-shaped extrusion profiling for housing materials), calendering (wide films and sheets such as agricultural films and PVC leather), injection and blow molding (except injection molding, because its melt viscosity is high). PVC materials have rather low densities, hence they offer relatively low material costs on a volume basis and hence are cost-effective. PVC is one of the major low-cost, high-volume commodity resins used today due to its economy and the excellent chemical and mechanical properties it provides.

Two main types of PVC resins are produced and processed:

1. Rigid PVC resins (unmodified PVC, uPVC), which have considerable strength and hardness; they are processed mainly by extrusion or molding to make pipes and conduits, fittings, window profiles, roof tiles, fences and various rigid automotive parts. Rigid PVC sheets can be welded easily to produce tanks, trays and troughs.
2. Flexible PVC resins, which contain various additives, mainly plasticizers, usually in high proportions to make them soft and flexible and heat and UV stable.

When plasticizers are added, flexible plasticized PVC (pPVC) is obtained with rubber-like elasticity, high tensile and fatigue strengths, which can be used specifically for industrial hoses, gaskets, elastic automotive parts and electrical cable covers, where elasticity is a must. pPVC also finds applications in film and sheets, flooring, shower curtains and synthetic leather products. In the 1970s pPVC was often used to make 'vinyl car tops', and it was also used to make vinyl records. PVC-based materials also have a key role in the production of medical and clinical devices; however, similar arguments are arising with regard to its safety issues (Latini *et al.*, 2010). Table 2.1 summarizes some characteristics of PVC.

PVC can be mixed mechanically with various substances rather easily, hence it has the 'ease of formulation' characteristics, because of the existing

Table 2.1 Some characteristics of (rigid) uPVC

Density (at 25°C)	0.5–1.45 g/cm^3
Specific gravity	1.3–1.7
Hardness durometer	R 90–115
Tensile strength	30–65 MPa (flexible: 7–25 MPa)
Tensile (Young's) modulus	2–4 × 10^2 MPa
Tensile elongation	20–190%
Compressive strength	50–90 MPa
Fatigue strength	17 MPa (after application of repeated stress by 10^7 times)
Impact strength (notched)	2–6 kJ/m^2
Service temperatures	–13°C (min.) to 70–80°C (max.)
T_g (glass transition temperature)	80°C
T_m (melting temperature)	240°C (decomposes)
Ignition temperature	455°C (inherently fire retardant)
Coefficient of thermal expansion (linear)	5 × 10^{-5} mm/mm°C
Resistance to acids (dilute/concentrated), alcohols, bases, aliphatic hydrocarbons, mineral oil	Excellent
UV resistance	Good
Water absorption (24 h)	0.04–0.4
Resistance to vegetable oil and oxidizing agents	Good
Resistance to aldehydes, esters, aromatic and halogenated hydrocarbons, ketones	Limited (poor)
Resistance to oxidation by atmospheric oxygen	Excellent (Durable)
Mechanical stability	Excellent (very low creep deformation) (Makino, 1998)
Dimensional accuracy for molded PVC products	High
Secondary processability (in welding, high-frequency bonding and vacuum forming, as well as 'on-site workability' properties)	Excellent

polar groups (chlorine). Mainly plasticizers and various additives and modifiers are used in PVC formulations to design the required physical properties of end products, such as improved flexibility, elasticity, impact resistance, anti-fouling, prevention of microbial growth, anti-misting, improved fire retardance, etc. The same polarity of chlorine also contributes to its ease of coloring, printing and adhesion. PVC is used in various decorative applications in buildings such as wall coverings and floorings by taking full advantage of its superior printability and ease of colorability with desired patterns and weatherability characteristics (Patrick, 2005).

2.3 Building applications of polyvinyl chloride (PVC)

Globally, over 50% of processed PVC is currently being used in construction, in products such as pipes, wiring, siding, flooring and wallpaper. As a building material, PVC provides economy, and ease of installation and replacement compared to more traditional building materials (e.g., wood, concrete, even clay) (Thornton, 2002).

2.3.1 PVC pipes

Because of its inherent water resistance, PVC is used to make raincoats and shower curtains and, of course, especially water pipes. PVC is extensively used for municipal water supply/sewage pipes, spouts, etc., since its mechanical properties such as tensile strength and tensile modulus are better than those of other general-purpose olefin plastics, and it is robust and durable. Home plumbing systems have different types of piping materials for different types of use, e.g., domestic water supply, waste drainage, appliances, irrigation and so on. PVC as a rigid plastic is used preferably in sanitary waste lines, vent pipes and drain traps for both residential and commercial applications. PVC rigid pipe can be easily cut (with a hacksaw or tubing cutter) and fitted, and it is often used to repair sections of broken old cast iron waste pipes. Its sections can be joined together mechanically (using plastic pressure fittings for later removal) or permanently (using the special chemical solvent) (Fig. 2.1).

PVC pipes are expected to last for a significantly long time (predicted to be up to or in excess of 100 years) under normal conditions, reducing both maintenance costs and environmental impact (Makino, 1998).

Global annual demand for plastic pipe, most of which is made of PVC, is predicted to reach 20.3 Mt (million tons) by 2015 with an annual increase of about 7% and with continued strong prospects in developing nations, particularly in China, which already accounted for 30% of the overall profits for plastic pipe between 2007 and 2012 (Anon., 2011c). In fact, generally increasing demand for PVC piping in China is primarily driven by

2.1 PVC pipe and fittings.

expansion in construction expenditures, as well as by the advances in consumer spending; and it would be good to remember that in 2005 China had already passed the US to become the largest consumer of PVC in the world (Anon., 2007a).

2.3.2 PVC profiles

Window and door profiles are other demanding applications for rigid PVC (uPVC), because of the high level of product performance required. uPVC profiles are used for window frames, doors, conservatories, fascias, skirting boards, architraves, soffits, guttering, rainwater systems, fences and decking, etc. PVC offers for all such applications a lightweight, maintenance-free and cost-effective alternative in a range of colors with an esthetic wood-grain finish, if needed, in addition to effective heat and sound insulation characteristics, so that it has already displaced traditional materials such as wood, steel and aluminum that had long been in use (Table 2.2). PVC window profiles are expected to last for more than 40 years under normal conditions, reducing both maintenance costs and environmental impact appreciably. As seen from Table 2.2, uPVC has the lowest values of k (and hence the highest values of R), meaning that it is a much more effective thermal insulator than aluminum, steel and wood.

Table 2.2 Some heat insulation characteristics of selected profile materials

Material	Conductivity (*k*) value	Insulative (*R*) values
uPVC	0.21(as a reference, for a perfect insulator, polyurethane foam insulation board, $k = 0.17$)	4.80
Wood (dry)	0.33	3.03
Aluminum (6061)	1160.00	0.00086
Aluminum (5052)	960.00	0.00104

Thermal insulation is characterized by the thermal conductivity (also referred to as the *k* value), which is the level of the speed at which heat travels through a material through conduction: the lower the *k* value, the better the thermal insulation. The reciprocal of *k* is *R*, which is frequently used to describe the performance of insulation materials: therefore, the higher the *R* value, the better is the insulation quality.

Impact strength is one of the key requirements in plastic profiles, and it is being improved by using certain additives in rather small quantities in PVC profiles, such as chlorinated polyethylene (CPE) and/or certain acrylic rubber-like compounds. In addition, nano-sized (precipitated) calcium carbonate ($CaCO_3$) particles are being applied to provide larger surface areas to improve their interactions with the PVC matrix.

2.3.3 PVC flooring and tiles

PVC flooring (or PVC floor coverings, vinyl–polyvinyl floors and tiles) is of great interest for residential uses such as in garages, basements, wetrooms, kitchens – almost anywhere where a durable floor is needed. PVC has been a popular flooring material in North America for over 40 years, replacing traditional linoleum (or lino) floor coverings (made from renewable materials such as linseed oil, pine rosin, cork dust, wood flour and mineral fillers). PVC tiles and floors can withstand the toughest environmental and heavy loading conditions, and their commercial and industrial grades are available for use in places such as offices and other heavy traffic areas (for both pedestrians and vehicles), sports areas, hospitals, etc. PVC floors provide waterproof and soundproof solutions. They are almost a natural choice in buildings with large floor spaces, such as schools, offices and public buildings, where durability and low maintenance are vital. PVC anti-slip mats are available. Vinyl flooring also offers an affordable and effective solution for places where sensitive electrical and computer equipment is installed and static charges are a big problem, with its additional 'antistatic' grades.

Most PVC floors are created through a process known as 'plastisol spread coating'. For this, the plasticizers are first combined with PVC powder to produce a liquid paste or 'plastisol' which is then applied in several layers, that is, the floor is composed of a foam core and a decorative and clear protective wear layer is built up on top. PVC floorings are predicted to last for at least 10 and up to 30 years.

PVC floorings should be elastic enough to provide flexibility and damping, and the material usually contains certain chemicals as additives to provide these properties. Plasticizers, mainly phthalate plasticizers, such as diisononyl phthalate (DINP) with 5–16 wt% and butyl benzyl phthalate (BBP) with 1.6–5 wt%, as well as others, have been used to help flexibilize the system. In addition, various organotin compounds, e.g. dibutyl tin (DBT) and tributyl tin (TBT) with concentrations of 38–560 ppm and 128–18,000 ppb, respectively, have been used as heat stabilizers (Allsop *et al.*, 2000). Most of these compounds are toxic and can leach or emit from the system to the surroundings, which has drawn particular concern. A more detailed account of these additives will be given in Section 2.4.

2.3.4 PVC siding

PVC (or vinyl or uPVC weatherboard) siding is a plastic cladding for the house, used for weatherproofing, insulation and decoration, externally. PVC siding has been the most commonly installed exterior cladding for residential construction in the US and Canada since the late 1950s. It is an engineered product with the possibility of a range of colors and finishes, used as an alternative to traditional sidings such as wood, aluminum and fiber cement.

Approximately 80% of PVC siding's weight is PVC resin, the rest being composed of additives that are needed for properties like color, opacity, gloss, impact resistance, flexibility, and durability for the system. Within these additives, small amounts of various plasticizers may be used to flexibilize the system, together with a number of stabilizers such as lead compounds. Additionally, vinyl sidings can release toxic fumes when they burn (e.g., in the case of fire), particularly dioxins. All of these raise considerable health concerns and will be discussed in more detail in Section 2.4.

2.3.5 Other PVC applications in construction

PVC liners

PVC liners use the advantage of combining good chemical resistance and good physical properties, along with their ease of heat or radiofrequency (RF) weldabilities. There are a number of applications of PVC liners, mostly as geo-membranes, such as in landfill liners, secondary waste containment liners, pond liners (for both hazardous and non-hazardous compounds), and liners for artificial lagoons, among others.

In addition to a number of such practical and important applications, flexible PVC liner systems that are used to insulate city potable water tanks have been shown to extend the life of these tanks considerably (Anon., 2008).

Geo-fabrics or geotextiles, which may be considered as another version of PVC liners, are systems associated with permeable fabrics which, when used in the soil, have the ability to separate, filter, reinforce, protect, or drain.

PVC wire and cable insulation (coatings)

pPVC is commonly used as an insulator on electric wires and cables to provide electrical insulation, where again health considerations related inherently to PVC as well as to the plasticizers and other additives used are under discussion.

Others

Tarpaulins are large sheets of strong, flexible, waterproof material, for which a cloth such as canvas is coated with plastic or latex. Commonly, the material used for tarpaulin systems is composed simply of outer sheet layers of PVC with the fabric layer inside.

Several other examples of the uses of PVC can be given: blinds, wallpapers, vinyl-backed carpets, fences and roofing membranes to reflect solar energy, mainly for the outside of the house. Vinyl (PVC) roof membranes have been used in commercial construction for over 40 years in the US and for even longer in Europe.

PVC is also used as a composite in portable electronic accessories or housings. Through a specific fusion process, PVC can also gain 'cleaning by absorption' properties to absorb dust particles and bacteria.

2.4 Health and safety concerns and polyvinyl chloride (PVC)

Two large and overlapping categories are generally used to classify chemicals that threaten human health:

1. Persistent bio-accumulative and toxic chemicals (PTBs)
2. Chemicals that mimic or block the action of hormones, also called endocrine disruptors (ECDs).

PTBs are of particular concern for human health, because they do not break down quickly in the environment (that is, they persist and can become widely dispersed over long distances by wind and water). And finally they become concentrated in tissues as they move up the food chain.

Persistent organic pollutants (POPs) are a common term, essentially synonymous with PTBs. The single international treaty attempting to limit the use of 10 specified chemicals primarily pesticides, is known as the POPs Treaty. Dioxins, to be discussed below, are perhaps the best known of the PTBs.

While ECDs are usually exogenous man-made industrial chemical products or by-products, occasionally they are also found in some plants and herbs. ECDs imitate or block the hormones of normal human physiologic regulation. The concept of ECDs is relatively recent, dating back to 1991. The term was first used to describe industrial chemicals found in the environment that appear to disturb the development and function of hormonal systems by participants in the Wingspread Consensus Conference in Wisconsin, USA, in 1991 (Anon., 1991). ECD is an important toxicological concept, but many still believe that evidence for ECDs causing disease in humans is contested. Several reviews of this topic are available, e.g. Taeusch *et al.* (2000) and Diamanti-Kandarakis (2009).

PVC is a sturdy, versatile, relatively low-cost material well adapted to use as a building and construction material. The use of PVC is complicated somewhat due to some of its properties being associated with possible toxicity. By-products that can be hazardous to human health are formed throughout the lifecycle of PVC, from its manufacture right through to its use and eventual disposal. These concerns have led some nations to limit or even completely ban the use of PVC. PVC manufacture and use is a contentious issue in the US and the EU, in particular. Environmental health advocates argue for severe limits to PVC use; while others, primarily in the chemical and building industries, support its use.

Health effects attributed mainly to PVC and related chemicals found in building materials include:

- Neuro-developmental problems including learning disabilities and autism
- A number of reproductive developmental problems including anatomic abnormalities such as hypospadius
- Altered male/female birth sex ratios at birth
- Preterm birth, early puberty and menstrual disorders
- A variety of cancers
- Impaired immune functions mainly connected to disorders such as asthma.

The question is how strong are these associations and how was the evidence developed.

2.4.1 Health and safety concerns related to the inherent chemistry of PVC

PVC is an organochlorine chemical (which is a carbon-based organic chemical with one or more chlorine atoms), which exhibits a number of important attributes shared by the class. Over three-quarters of about 40 million tons of chlorine produced annually is used in the production of more than 11,000 different organochlorine chemicals, including plastics (i.e., PVC), various pesticides, chemical intermediates, etc., and thousands of additional organochlorines are formed as by-products (during manufacture, use, and disposal of organochlorine-containing products).

There are three main characteristics of organochlorines that help to make them particularly troublesome, and have to be considered:

1. Chlorination changes the chemical stability of organic chemicals, making many organochlorines highly persistent in the environment. Even dilute discharges of such substances can accumulate in the environment over time, reaching measurable levels in air, water, and sediments. Persistent substances are transported long distances through the atmosphere and can be distributed globally, accumulating even in the remote regions of the Canadian and European Arctic, the rainforests of South America, and the Pacific islands.
2. Many organochlorines are strongly lipophilic – that is, they are highly soluble in fats (but not in water), so they preferably can accumulate in fatty tissues. In addition, these fat-soluble substances that resist degradation (and excretion) can magnify in concentration as they move up the food chain; organochlorine body burdens in carnivores are typically millions of times greater than the levels found in ambient air, soil, and sediments. Hence the human population, at the apex of the food chain, is bound to be particularly contaminated,
3. Finally, organochlorines tend to be considerably more toxic and more carcinogenic than their non-chlorinated analogs. It has long been known that some organochlorine chemicals produce a variety of adverse health impacts, including cancer, organ damage, and damage to reproductive systems, with neurological and immunological toxicity, in particular during sensitive periods of fetal and infant development. Within the several hundred organochlorines that have undergone toxicological testing to date, all organochlorines examined have been found to cause one or more of a wide variety of adverse health effects, often at very low doses. A large number of organochlorines are endocrine disrupters

(ECDs) that can mimic or otherwise interfere with hormone action, raising the possibility of severe long-term effects on reproduction, development and behavior.

In addition, when PVC is burned, some chlorines are easily released (which is the reason why PVC is not flammable and has inherent flame retarding properties, because chlorines react with radicals produced during the process, hence inhibiting the process), producing toxic hydrochloric acid (HCl) fumes. When hydrogen chloride gas enters the lungs, it becomes an extremely caustic acid that can result in internal chemical burns in a person who inhales it. This acid smoke is so potent that it can even kill a person inside a house fire, hence it will be the main danger when a PVC compound is combusted.

Combustion of PVC produces not only smoke of toxic acidic HCl gas and lead (the latter from stabilizers), but it can also produce dioxin-like products in the gas phase. Dioxin is an organic chemical with a pair of benzene rings, two oxygen and four chlorine atoms (the well-known DDT and dioxin share several characteristics chemically, primarily that both are toxic even in very small quantities). Dioxin and dioxin-like compounds (DLC) are among the products of burning of PVC, e.g. from incineration of waste PVC in domestic garbage or from house fires, as well as by-products of various other industrial processes. They are commonly regarded as highly toxic compounds and POPs, although their toxicity is not agreed by the whole scientific community. Dioxin was used through the infamous 'Agent Orange' by the US armed forces during the Vietnam War.

Within the dioxins, there are:

- Polychlorinated dibenzo-p-dioxins (PCDDs), known simply as dioxins. There are 35 PCDDs, and seven of them are specifically very toxic.
- Polychlorinated dibenzofurans (PCDFs), or simply furans. There are 75 PCDFs, and 10 of them have highly toxic dioxin-like properties.
- Polychlorinated biphenyls (PCBs), which have dioxin-like properties.
- Finally, there is dioxin itself, the basic chemical unit of the more complex dioxins. This simple compound is not persistent and has no PCDD-like toxicity.

The Greenpeace group has advocated the complete phase-out of PVC globally because according to their claim dioxin is produced as a by-product during vinyl chloride monomer (VCM) production, as well as from the incineration of waste PVC in domestic garbage and through landfill and home fires. The lifecycle of PVC begins with the manufacture of VCM gas. VCM, the monomer, which is toxic (see below), is then polymerized into the polymer PVC and then formulated with a number of different additives into final products.

2.4.2 Health and safety concerns related to the VCM and additives

The conversion of PVC into more useful final materials requires the incorporation of a number of different additives, i.e., additives that serve as plasticizers needed to flexibilize the system, heat and UV stabilizers for stabilization, fillers either to improve mechanical and physical properties or to make the system more cost-effective, flame-retardants to improve flammability characteristics, biocides for sterilization and to add anti-microbial properties, pigments, etc. These additives and other processing aids are physically mixed into the PVC matrix, but they are not chemically bound. Table 2.3 presents additives used in PVC, their functions and substance classes used.

Table 2.3 Examples of additives and their functions in PVC

Additive	Function	Substance classes used
Plasticizers	Protection of elasticity	Phthalate esters: Di(2-ethylhexyl) phthalate (DEHP) Di-isononyl phthalate (DINP) Dibutyl phthalate (DBP) Benzylbutyl phthalate (BBP) Di-isodecyl phthalate (DIDP) Di-*n*-octyl phthalate (DNOP) Di-isopentyl phthalate (DIPP) Other plasticizers: Adipic acid esters, e.g. di(2-ethylhexyl) adipate Citric acid esters, e.g. acetyl tributyl citrate Cyclohexanedicarboxylate esters Alkylsulfonic acid esters Dipropylene glycol dibenzoate (DGD) Trimethyl pentanediol diisobutyrate (TXIB) Sebacates Azelates Chlorinated paraffins
Stabilizers	Stabilization against the influence of light and temperature	Cadmium stabilizers (forbidden in the EU) Lead stabilizers Orgotin stabilizers Calcium / zinc stabilizers
Pigments	Coloring of plastic products	Inorganic pigments (e.g. titanium dioxide, iron oxide, chromium oxide and iron blue, ultramarine and soot pigments), lead chromate

Table 2.3 (*Continued*)

Additive	Function	Substance classes used
Fillers	Improving workability and wear performance (comprise up to 50% of the PVC material)	Calcium carbonate (chalk) Magnesium silicate hydroxide (talc) Barytes
Flame retardants	Increasing fire resistance	Aluminum trihydrate (ATH) Phosphoric acid esters Antimony trioxide (ATO) Chlorinated paraffins
Lubricants	Improving flow during the thermoplastic processing (comprise up to 3% of the PVC material)	Waxes, etc.
Antistatic agents	Reducing electrostatic charging	Perchlorates, etc.
Surface active agents	Reducing surface tension	Esters of long chain alcohols, etc.
Reinforcement	Reinforcement for expanded PVC floorings	Glass fibers, etc.

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In addition to these intentional additives used at the processing stage, there is the possibility of having unintentional additives (e.g., the chemical impurities in the intentional additives used) and 'interaction additives' (new chemicals produced from chemical reactions between the additives in the system). As a result, any of these chemicals (from intentional, unintentional or interaction additives) can be easily released (leached or emitted) from the product into the environment, and since most of them are toxic, this possibility should also be considered in determining the overall toxicity of PVC (Akovali, 2007).

VCM, the monomer

Residual VCM, the monomer of PVC, can be left in the polymer matrix unreacted as an 'impurity' after the polymerization reaction, usually with a concentration of less than 1 ppm. This residual VCM can leach from any PVC material, e.g. PVC pipe, to water. In fact, migration of VCM into drinking water from PVC bottles (Fayad *et al.*, 1997) and from PVC water pipes (Al-Malack, 2004; Bellen *et al.*, 1987) has been reported; and different factors that can affect the accumulation of VCM in PVC piping used in drinking water distribution systems are discussed (Walter *et al.*, 2011).

VCM is a strong toxic chemical that can cause a rare liver cancer, angiosarcoma (also known as hemangiosarcoma), and blood tumors. VCM is toxic both by inhalation (affecting the human reproductive system, with serious changes in spermatogenesis) and by contact with skin (it is a severe irritant to skin, eyes, and mucous membranes, causing skin burns) or if swallowed (moderately toxic by ingestion). VCM's carcinogenic effect on humans was first understood and realized during the 1970s, through the workers in PVC factories, who were exposed (routinely and for long times) to very high levels of VCM because of the 'open-loop' polymerization system they were using. Obviously, such toxic effects were not expected at all from VCM in the near past, because until its toxic effect was clearly understood, VCM was being used in aerosol spray propellants (e.g. in beauty parlors by hairdressers) and as an inhalational anesthetic at large for years, until the US FDA banned VCM use in 1974. Strict workplace exposure limits were established by the Occupational Safety and Health Administration (OSHA) by then. The occupational limits for VCM currently are set at 1 ppm (averaged over an 8-hour period) and 5 ppm (averaged over any period not exceeding 15 minutes), with annual maximum exposure limit of 3 ppm. The 1997 European Pharmacopoeia requires a maximum of 1 ppm of VCM residual in virgin PVC. By the end of 1995, 175 cases of angiosarcoma (due to VCM) had been diagnosed worldwide (Mulder and Knot, 2001).

Plasticizers

Various plasticizers are used in PVC formulations to create a softer and more flexible plastic, hence permitting its use in hoses, clothing (artificial leather), flexible toys and roofing membranes. More than 300 different types of plasticizers are known so far, and 50 of them are in commercial use. The most commonly used plasticizers are esters, such as adipates, mellitates and phthalates, the latter being the most widely used.

Phthalates are esters of phthalic acid and are used as plasticizers to increase the flexibility, softness and durability of PVC building materials. Phthalates have a clear syrupy consistency and in PVC they create a distinctive 'new car' odor. When added to PVC, they do not chemically combine or bond with the vinyl chloride, but are mechanically inserted between the long polyvinyl molecules, hence allowing them to slide one against another, 'flexibilizing' the system. Depending on the formulation of the PVC product, phthalates are generally used to make up 40–60% by weight of the final product. By 2010, it was estimated that more than 200 million kg of phthalate plasticizers were being used annually in PVC building materials.

There are three phthalate plasticizers that are most commonly used for PVC:

- Di-2-ethylhexyl phthalate (DEHP)
- Di-isodecyl phthalate (DIDP)
- Di-isononyl phthalate (DINP).

Of these, DEHP is the most common, primarily because of its low cost and efficiency; but it is the most toxic, and is the best-studied plasticizer. It is suspected that mono (2-ethylhexyl) phthalate (MEHP) is the major breakdown product of DEHP that both affects the respiratory system and causes asthma. DEHP is commonly used as a proxy for the toxicity and exposure assessments of other phthalates. In addition, benzylbutylphthalate (BBP) is used as a plasticizer specifically in foam flooring materials.

2-Ethylhexanol-ethyl-1-hexanol (2E1H), usually detected in indoor air at relatively high concentrations, is considered as a product of DEHP plasticizer in PVC flooring material, and from other existing compounds with the 2-ethyl-1-hexyl group (e.g., in the adhesive). 2E1H is considered to be one of the causes of bad odor in indoor air and sick building syndrome (Satoko *et al.*, 2009).

Toys made from pPVC with 10–40% phthalate plasticizers have been subject to an 'emergency ban' in the EU since the end of 1999.

Phthalates have high affinity for suspended particles and a study showed that when they vaporize into air, they are absorbed by suspended particles in air and in sediment dust samples from homes (Oie *et al.*, 1997). Hence they can migrate easily to sedimented house dust. Washing has also been shown to release phthalates into the water (Moller *et al*,. 1996).

Years ago, Swedish researchers observed that male workers in PVC plants have a high risk of developing 'seminoma' (a form of testicular cancer) in Sweden, with a probability six times higher, which was linked to the DEHP, which is a suspected ECD agent.

Another study showed that when DEHP is present at seven times the normal level which was the case for some Puerto Rican girls aged between 6 months and 2 years, there are cases of premature breast development (Lomenick *et al.*, 2010; Swan *et al.*, 2005).

A 1999 study made in Oslo, Norway concluded that young children may absorb phthalates from vinyl floor coverings, and that these children have almost double the chance of developing bronchial obstruction and symptoms of asthma. Research shows that DEHP can leach and emit easily, e.g. from PVC flooring, and it is found mostly in dust particles in the home and in wash water from PVC floors whenever this happens. Hence any hazardous chemical in PVC flooring that leaches out leads automatically to human exposure in the indoor environment.

A good understanding of the toxicology of phthalates has been developed from studies using cell cultures, animals and human exposures. Human studies are primarily case control and ecological designs. So far, no controlled trials on humans have been performed for obvious ethical reasons, as the commonly used phthalates are commonly accepted as toxic.

There has been controversy for many years concerning the health hazards of phthalates, in particular DEHP. Strong criticism against any use of phthalates are expressed by certain non-governmental organizations such as Greenpeace and Friends of the Earth (Higgs, 2005).

In both wildlife and laboratory animals, phthalates have been linked to a range of possible biochemical effects (mainly reproductive health effects and autism) with the claims that most of them can function as ECDs. There have also been other claims such as that they are cancer-causing agents, specifically in liver and kidneys. In any case, negative health effects of phthalates in general have been suspected due to the existence of short ester chains (< C9) in them.

In 2000, the International Association for Research on Cancer (IARC), attached to the World Health Organization (WHO), reduced the carcinogenic rating of DEHP from 2B to 3, meaning a change of its standing from 'possibly carcinogenic to humans' to 'cannot be classified as to its carcinogenicity to humans' (Anon., 2000).

Since September 2004, the EU has not allowed the use of some phthalates (DEHP, DINP, DIDP) specifically in toys and personal care products made for children (where children can put the product in their mouths). The EU put forward the year 2002 as the key milestone to complete phthalate risk assessment. Two phthalates (DINP and DIDP) are shown to cause accelerated dehydrochlorination of PVC at high temperatures (Patrick, 2005).

Estimates of human health effects of DEHP have been used in risk assessment studies of PVC building materials. A recent US Green Building Council assessment of PVC building materials uses a combined lifecycle and risk assessment technique and uses data from a study by the Air Resources Board of California of indoor air samples of inspired phthalate concentrations from 125 homes in southern California (USGBC, 2007).

Stabilizers

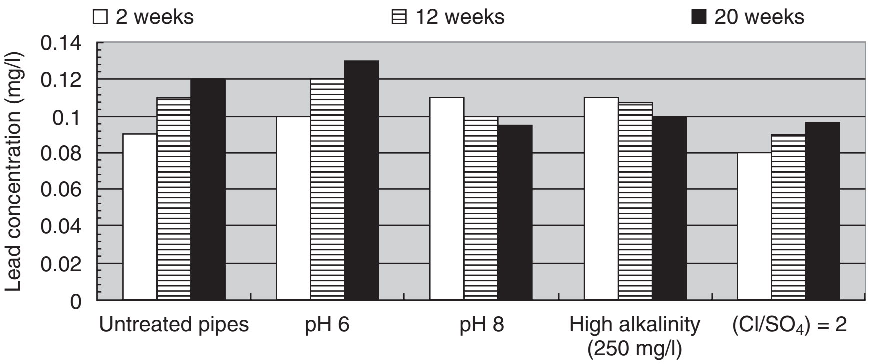
Stabilizers are 'intentional additives' used to prevent environmental effects (of heat, UV light, etc.) on the polymer. They are added to plastics to afford protection against heat (thermal), UV and mechanical degradation of the polymer during both processing and use. They can function as antioxidants, heat (thermal) and photo/light (UV) stabilizers, flame/fire retardants and oxygen scavengers. For PVC, the thermal decomposition temperature is close to the process temperature, hence use of proper heat stabilizers is essential both during its processing and afterwards.

Some of the stabilizers can contain certain heavy metals or their ions (e.g., stabilizers for PVC window profiles and pipes are mostly lead based or barium, cadmium, or zinc compounds, and in addition organonickel compounds are used for UV stabilization specifically), which can pose health hazards.

The main heat stabilizers available and used for PVC are:

- Compounds of lead (mainly basic lead sulfate and lead stearate). All forms of lead are extremely toxic to humans because of their cumulative effects. It has been shown that lead causes brain damage, learning disabilities, high blood pressure and even miscarriages. Exposure to lead-contaminated water is specially a persistent universal problem with a significant health risk. When ingested through the gastrointestinal tract, lead accumulates in organs and bones, and finally causes a number of diseases ranging from anemia to nervous system degeneration (Godwin, 2001). WHO recommended 10 μg/l for lead in drinking water (WHO, 2006).
- Organotin compounds, mainly mono-butyltin (MBT), dibutyltin (DBT) and tributyltin (TBT). In addition, dimethyltin (DMT) is another organotin detected in domestic water supplies arising from stabilizers used for PVC and chlorinated PVC (CPVC) products (Ehman *et al.*, 2007). There are suspicions that organotin compounds can be persistent and toxic to the central nervous and immune systems and to the liver (Korgiesen and Rice, 1998). Organotin compounds represent about 9.3% of European consumption of stabilizers (CEC, 2000).
- Cadmium (Cd) and its complex salt systems. Cd is an accumulative poison in the list of the top 10 hazardous pollutants of UN Environmental Programs; it can cause kidney damage and anemia, and once absorbed, can remain for 30 years in the human body. Inhalation of cadmium oxide fumes is the greatest hazard with a number of fatal consequences.
- Antimony (Sb) is used in PVC to enhance the flame-retardant effect of chlorine.
- Organochlorines are usually needed to enhance the flame retardancy characteristics as well as the impact strength characteristics of PVC.

There are various reports of the leaching of some of these toxic ingredients to the surroundings, such as tin compounds from PVC pipes (Sadiki, 1996; Sadiki and Williams, 1996, 1999; Nikolaou *et al.*, 2007; WHO, 2004), and other compounds (NIEH, 1997). For PVC products that are meant to be rigid, like vinyl siding or rigid water pipes, usually plasticizers are not of



2.2 Mean concentrations of lead release from PVC pipes (72 h stagnation) (from the paper by Lasheen *et al.*, 2008. Kind permission of Elsevier Ltd, UK, is gratefully acknowledged).

prime concern, but stabilizers are, e.g. lead compounds in stabilizers. In one study, it is shown that appreciable amounts of lead compounds are leached from PVC rigid water pipes (Al-Malack *et al.*, 2001; Lasheen *et al.*, 2008). Mean concentrations of release of lead after 72 h of stagnation, from this study, are presented in Fig. 2.2.

Since stabilizers used for PVC are usually in suspended form in the matrix, toxic ingredients can reach the exterior of the surface of the PVC in time, under either static-normal standing or dynamic operational conditions accelerated by temperature, by simple diffusion. After that, they can be transferred either by evaporation/sublimation or by simple leaching, or both.

It is expected that toxic effects of these additives individually, and those from the matrix material (PVC) itself, can probably have a 'combined effect' in the end: PVC flooring is expected to have both the 'plasticizer' and 'organotin' problems. Considering the fact that flooring usually has a substantial surface area within the home, these effects can be critical. In addition, if combustion of a vinyl floor is considered (as in a house fire or in cases of incineration), in addition to the 'plasticizer' and 'organotin', there will be the additional problem arising from the combustion of the matrix PVC itself.

Nevertheless, since the early 1990s the EU has restricted the use of Cd as a colorant and as an additive in plastics; and its use in PVC was stopped already by 2001 by most of the industry. There is an EU limitation for the use of cadmium from December 2010, with a concentration limit of 100 ppm for pipes, flooring and cabling but not for windows and other profiles, and roofing, introduced under the REACH legislation, which enables restrictions to be imposed on specific hazardous substances (*Chemistry World*, 2011). However, it does not apply to cadmium in electrical and electronic products which are controlled by the Regulation on Hazardous Substances (RoHS) directive.

Lead will be phased out by 2015. In other cases, research is continuing to ascertain for certain which plasticizers used in PVC are carcinogenic or have ECD properties.

PVC is inherently flame retardant, but in some cases it is needed to improve this property and flame-retardant additives are used. Chlorinated polyethylene, CPE, is usually the most suitable, but in this way, the chlorine content in the system increases and problems related to human health become a more serious issue.World demand for flame-retardant additives, in general, is expected to reach 2.2 Mt by 2014 (Anon., 2011a).

2.4.3 Health and safety concerns related to the disposal and recycling of PVC

There are three ways to recycle or dispose of PVC:

- Recycling by the direct recovery of scrap or waste plastics and reprocessing the material into useful products (mechanical recycling)
- Conversion of scrap or waste plastics into other useful chemicals or energy
- Disposal by simple landfill.

PVC can be processed into a wide variety of short-life or long-life products. With increasing consumption in recent years, the quantity of used PVC items entering the waste stream is gradually increasing; and there is considerable public concern about the problem of plastic wastes, specifically of PVC (Sadat-Shojai and Bakhshandeh, 2011).

Around 0.6% of the European domestic waste stream of 120 Mt per year is PVC waste. In 2001 PVC producers set a target of recycling 200,000 tonnes/year of PVC by 2010 (*Vinyl 2010*, 2001).

Recycling of PVC wastes by any of these methods has been difficult to achieve until very recently on the industrial scale, and the processes were also of interest environmentally and were criticized due to the expected possible health and safety concerns. Recycling of clean and homogeneous post-consumer PVC (or factory scrap) by direct reprocessing is possible and should be 'health and safety feasible', e.g., rigid PVC can be recycled and new pipes and profiles can be produced, although the process is not economic: recycled PVC is more expensive than the virgin resin.

Within the last decade, several viable methods have been developed for recycling of scrap PVC, such as the one developed in Europe called 'Texiloop', based on a technology already applied industrially in Europe and Japan called 'Vinyloop', consisting of recovery of PVC from composites through dissolution and precipitation via a closed loop system (Texiloop, 2002). This type of recycling is expected to cause no health concerns, but it is certainly not economic.

Recycling by burning waste PVC has been heavily criticized, because of the high probability of emission of chlorinated by-products, e.g. dioxins. In fact, burning waste PVC seems to be the best option for energy recovery (Katami *et al.*, 2002; Wagner and Green, 1993). In this case, plastic, being the most important constituent of the waste, would provide the calorific energy necessary for burning. The effective heat of combustion of PVC is 17.95 MJ/kg. However, incinerators burning large amounts of waste PVC are shown to release large amounts of dioxin into the air at the same time (Beychok, 1987; NREL, 1993; Costner, 1995; Anon., 2007b).

In addition, it has been shown recently that TiO_2 encapsulated PVC (TEPVC) has a lower emission of toxic chemicals upon waste incineration as compared to PVC, most probably owing to the catalytic oxidation and decomposition of all toxic chemicals by the encapsulated TiO_2 nanoparticles. This certainly presents a potential application as an eco-friendly alternative to conventional PVC (Hyonggoo and Seung-Yeop, 2011).

An experiment to find out how much energy can be recovered from plastic material that has been reused and recycled has been carried out (Anon., 2011b).

Discarding waste PVC in landfill is not a real long-term solution, and the use of landfill for waste PVC should be the last option, because of the economy of the material involved. In addition, PVC is not inert in landfills, and there are concerns that various toxic additives can leach out and poison the soil, as well as water sources. According to some critics, PVC can increase the toxicity of any leachate. While PVC is not biodegradable, some of its additives are.

2.4.4 Bio-monitoring

The second industrial revolution spawned an immense chemical industry that provides materials now used in virtually every sector of commerce. Industrial processes into fuels, plastic, pesticides, cosmetics, food additives, and pharmaceuticals transform petroleum and other materials. In the United States, some 70,000 individual industrial chemicals are registered with the Environmental Protection Agency (EPA) for commercial use and are sold in the marketplace, some in billions of dollars per year. Only a very small fraction of these substances have been characterized for potential biological activity or human toxicity, and approximately 1500 new chemicals are introduced into the market each year. Thousands more novel compounds are generated as by-products of industrial processes or as degradation products and metabolites of other synthetic chemicals; even fewer toxicological data are available for these substances. PVC is a very good case in point.

Residues of man-made substances can now be found in the air, soil, water, and food web in the most remote reaches of the planet. Pollutants that are distributed ubiquitously result in universal human exposure through inhalation, drinking water, and the food supply. Some of the substances to which the general human population is exposed resist metabolism and excretion and therefore accumulate in body tissues. The quantity of an exogenous substance or its metabolites that has accumulated in an individual or population is defined as a body burden.

Body-burden estimation

An individual's body burden of a pollutant is estimated by measuring the concentration of that substance in one or more tissues, usually by gas chromatography/mass spectrometry (GC/MS). Chemical body burdens are complex and dynamic in a number of ways, and these characteristics make a full characterization of the general public's body burden exceedingly difficult. First, the body burden of a pollutant is not stable over time. It reflects a dynamic balance between the amount taken in and the amount excreted or metabolized into another material. Many industrial chemicals, like formaldehyde, benzene, and some pesticides, are taken into the body but are broken down and rapidly excreted or metabolized, producing a negligible long-term body burden, although levels after an acute exposure may be high. Chemicals that are persistent are those that resist metabolic alteration and excretion and/or are tightly bound to the tissues in which they are stored.

Second, body burdens are not distributed homogeneously within an individual: the partitioning of a pollutant among various tissues and fluids reflects the substance's degradability and affinity for fats, minerals, and other endogenous materials. Metabolic models have been developed for a number of toxic chemicals. These models summarize available knowledge about the metabolism of a specific chemical and predict the distribution of the chemical in the body and the rate at which it will be eliminated.

Third, the body burden of an individual in today's environment consists of hundreds of synthetic substances. The ability of chemical analyses based on GC/MS to characterize the full range of contaminants is limited in a number of ways. Compounds can be identified only if they are present in concentrations above a detection limit (usually in parts per trillion or billion). Substances present in very low quantities will not be detected, but if there are hundreds or thousands of them, together they may make up the bulk of the total chemical burden. Moreover, routine analyses can identify only compounds that can be matched against a reference database of chemical signatures, so substances that are not yet in the database go uncharacterized. Thus, novel or exotic compounds, such as many industrial by-products, environmental breakdown products, and metabolic products, will remain unidentified in even the most rigorous analysis. It has been estimated that the fatty tissues of the US general population contain at least 700 contaminants that have not yet been chemically characterized.

Bio-monitoring programs in the US

The human body burden of specific industrial substances has been well characterized in selected populations with high exposures, such as chemical accident victims, agricultural workers, workers in chemical and incineration industries, military personnel exposed to Agent Orange, and persons highly exposed to environmental chemicals through their diet or specific contaminated food. In addition, numerous studies have sought to identify specific compounds in samples drawn from individuals in the general population with no known special exposures.

Bio-monitoring surveys have studied broad samples of the US population. The National Health and Nutrition Examination Survey (NHANES II) studied lead and pesticide residues in blood during the period 1976 to 1980. In this national sample of nearly 6000 people aged 12 to 74 years, 36 pesticides and pesticide metabolites were quantified.

In 1991, a committee of the National Academy of Sciences called for a national program of monitoring body fluids from the general population for the presence of a list of target substances, based on a standardized protocol. Subsequently, the National Center for Environmental Health (NCEH), a division of the US Centers for Disease Control and Prevention (CDC), initiated the National Report on Human Exposure to Environmental Chemicals. Each year, the NCEH bio-monitoring laboratory will measure and report the exposure of a representative sample of the US population – a subsample of the ongoing National Health and Nutrition Examination Survey (NHANES) – to a number of priority toxic substances. In 2001, the CDC issued its first report from the National Report on human Exposure to Environmental Chemicals program.

A particular value of this national bio-monitoring program is its capacity to establish reference ranges for a large set of toxic chemicals. A reference range is defined as the concentration of a particular substance that is expected to be present in the general population with no unusual chemical exposure. The reference range is the standard against which a measuring laboratory can say that results for any group or individual are high, in a 'normal' range, or low. For materials like lead, cadmium, and some pesticides, good reference values exist because large numbers of persons have been studied using well-standardized and reproducible methods. For many other substances, laboratory methods have varied over time, and few large nationally representative populations have been studied.

'Normal' body burdens

All humans are now exposed to organochlorines and other industrial chemicals in drinking water, air, and food. For bio-accumulative compounds, including dioxins, PCBs, and many pesticides, the food supply is the major source of exposure. Over 90% of the average American's dioxin exposures, for example, come through the diet. Animal foods – meat, dairy, fish, and eggs – contain the highest concentrations of dioxin, but smaller exposures also occur through grains, fruits, and vegetables and their oils. For the more volatile and less bio-accumulative chemicals, such as solvents, disinfection by-products, and pesticides in groundwater, exposures via air and water play more important roles. Direct exposures to organochlorines also occur via consumer products, home pesticides, dry-cleaned clothing and commonly used building materials.

As a result of these universal exposures, the general population now carries a body burden of numerous organochlorines. Over 190 synthetic organochlorines have been identified in samples of tissues and fluids drawn from the general populations of the United States and Canada. The studies on which this list is based are subject to the limitations discussed above, but they do indicate that a very large number of synthetic substances found in the environment and food supply have accumulated in the bodies of individuals who have had no special chemical exposures. As one might expect, the list includes the best-studied organochlorines: dioxins, PCBs, and restricted pesticides. Like the ambient environment, however, the bodies of the general human population contain a representative sample of the full range of organochlorines, from simple chlorinated refrigerants and solvents used for cleaning, coating, and degreasing, to little-known specialty chemicals, by-products, and second-generation pesticides. The concentrations are typically small, ranging from the low parts per trillion to the high parts per billion, but they indicate widespread exposure and a continuing internal dose of a variety of compounds, many of which are known to cause health damage.

It is now 'normal' for the general population to have body burdens of industrial chemicals and metals, in the sense that no reference or control population can be found without these exposures. But the existence of an appreciable body burden of industrial chemicals is a relatively recent phenomenon. Lead and other metals have been measured in human tissue since the 1920s. Dioxin is non-detectable or present at only a very small fraction of current concentrations in preserved human tissue samples from pre-industrial times.

2.5 Alternatives to polyvinyl chloride (PVC)

There are several alternatives available for most construction-related uses of PVC, some realistic and some hypothetical. To begin with, several databases, such as those offered by the Healthy Building Network (HBN, 2004) and Greenpeace (Greenpeace, 2004), can be mentioned that list some of these alternatives.

A large number of construction projects, including the Sydney 2000 Olympic Stadium and the new EPA headquarters in Washington, DC, have been constructed using little (or almost no) PVC. In each case and in principle, alternatives to PVC do exist, some being long-established and traditional while others are rather new. For example, among the former, for piping material there are chromed brass (for waste line pipes), chromed copper (for water supply), galvanized iron (for water supply and drainage), rigid and flexible copper or CPVC and PEX crosslinked PE (for water supply) and black iron (for gas).

In general, acrylonitrile butadiene styrene (ABS) and high density polyethylene (HDPE) can be used as general replacements, while polypropylene (PP) is suggested for extruded profile replacement applications. On the other hand, there is an ongoing continuous search for new replacements; for example, Ferro Corp, USA, has introduced two new non-lead heat stabilizers for wire and cable coating applications (Anon., 2004), and DuPont, USA, has recently introduced a chlorine-free floor tile to compete with vinyl and vinyl composite tiles.

Certain alternative plasticizers are used with the aim of making PVC compounds safer; however, these alternatives are more expensive and sometimes their technical performance is not as good as those obtained with the common phthalate plasticizers; in addition, it is not known for sure whether or not these alternatives can reduce health risks.

One such alternative is soybean oil. In the US, vegetable oil plasticizers already represented about 15% of the market in 1996. Soybean oils are more expensive than phthalates, but they provide the following advantages:

- They confer stability (they eliminate the need for additional heavy metal stabilizers).
- They do not leach out easily from the plastic, hence they also help to extend the life of the PVC product indirectly.

The complete isosorbide family and its esters are also another green alternative recommended as plasticizers: their toxicity data showed no acute toxicity, no sensitization, no mutagenic effects (Ames test), and no estrogenic effects (Kimpeks).

As far as the hepatotoxicity of PVC plasticizers is concerned, trioctyltrimellitate (TOTM) is suggested in place of DEHP. TOTM is less toxic to certain animal species, and there is recently an increased market for di-isononyl phthalate (DINP) for the same replacement. The US Consumer Product and Safety Commission accepted that there is no danger posed by some phthalate plasticizers like DINP. Meanwhile, while the debate in the US continues, in the EU producers have already begun replacing DEHP by its alternatives, with phthalates like C9 and C10 since 2000, and one of the main producers of DEHP, BASF in Ludwigshafen, Germany, shut down their factory during 2005, though they decided to continue offering similar production in Asia (Anon., 2005). However, at the moment, DEHP is the only phthalate that has European Pharmacopoeia approval for its use in flexible medical devices (Wang and Storm, 2005; Patrick, 2005).

Replacement of PVC or its additives with green alternatives is still a very active ongoing subject. A recent questionnaire asked PVC users to vote which alternative for soft PVC fits best with their requirements, and the alternatives suggested were olefinic elastomers, styrenic elastomers, other olefins, PLA and its blends, starch blends, and others (Omnexus, 2011).

As mentioned above, a very recent study related to TiO_2 encapsulated PVC (TEPVC) showed lower emission of toxic chemicals in waste incineration as compared to PVC alone most probably because of the catalytic oxidation and decomposition of all toxic chemicals by the encapsulated TiO_2 nanoparticles. This new nano technique certainly presents a potential new opportunity and a new eco-friendly alternative to conventional PVC, as converting and modifying PVC itself to a 'green' plastic (Hyonggoo and Seung-Yeop, 2011).

2.5.1 Analysis of alternatives

Risk assessments have been performed to quantify potential risks of developing adverse health effects following exposure to toxicants associated with building materials including phthalate and VCM.

Lifecycle assessment

As discussed above, the hazards from PVC must be approached from an integrated understanding of the full lifecycle of a material like PVC, including supply chain processes and materials, manufacture and installation through all the end-of-life fates including by-products, wastes and emissions at each stage. The obvious complexities of such assessments are obviously enormous. But science, design, and regulatory communities have a growing awareness of the need for such analysis.

A recent and rigorous lifecycle assessment of PVC as a building material was commissioned by the US Green Building Council and completed in

2007 by Norris and his colleagues. In 2000 the Council decided that it needed a technical basis for offering credit in its LEED (Leadership in Energy and Environmental Design) system for avoidance of PVC materials. The resulting study is titled ‘Assessment of the Technical Basis for a PVC-related Materials Credit for LEED’. To compare the impacts of alternative material choices, two assessments were performed for each material in four applications: siding, piping, flooring and window frames.

A lifecycle assessment attempts to characterize and quantify all of the resource and pollution flows (inputs and outputs) associated with a particular material (PVC or an alternative) over its entire lifecycle: manufacture, use, reuse and disposal. The individual inputs and outputs are quantified in a lifecycle inventory and then characterized by their estimated contribution to environmental and health impacts. The study used an EPA system of categories and impacts including environment, ecosystem and human health impacts. A database of approximately 2500 publications was assembled and reviewed for the analysis. The database alone is a unique resource from this study. In addition to the LCA, three separate risk assessments were performed, including both cancer and non-cancer effects, on:

- Occupational health risks in PVC and alternatives manufacture
- Exposure to phthalates in residential indoor air and dust
- Residents exposed to VCM.

The findings are not easily summarized. The authors chose to frame the study’s goal (or null hypothesis, if you will) as ‘to determine whether, for the applications included, the available evidence indicates that PVC-based materials are consistently worse than alternative materials in terms of environmental and health impacts’. The results are very much qualified by ‘it depends’ statements. Across the four applications – windows, pipe, siding and flooring – PVC is not the worst alternative in the cradle-through-use portion of the lifecycle, but across the full lifecycle, including end-of-life incineration and dioxin production, PVC is in general the worst alternative.

Other analyses

LCA results can be dramatically altered or even reversed by the effects of assumptions in the design of the analysis and the uncertainty or unavailability of data. A case study of an LCA performed by the Vinyl Institute and several vinyl flooring manufacturers is presented in which the result appears to rate vinyl composition tile as having 3.98 times the (negative) environmental impact of linoleum, but only after the use of weighting schemes and the use of dioxin flow data that does not reflect total and so far unmeasured releases at such sources as landfill fires.

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2.6.1 Some related web-sites

ACE (Alliance for a Clean Environment): http://www.acereport.org/orgs.html
Healthy Building Network: www. healthybuilding.net
The Vinyl Institute: http://www.vinylinfo.org/
The Vinyl Siding Institute: http://www.vinylsiding.org/about/
WHO (World Health Organization) IARC (International Agency for Research on Cancer), Lyon, France: The USGBC document; An analysis by the Healthy Building network; http://www.pvc.org/The-PVC-Industry/ (EVCM – The European Council of Vinyl Manufacturers – represents the 13 European PVC resin-producing companies that produce 100% of the PVC resin manufactured in Europe.)