2 Thermoplastic powder coatings

The first powder coatings produced were based on thermoplastic polymers which melt at the application temperature, and solidify upon cooling. Several factors such as relatively simple methods of manufacturing and application, no involvement of complicated curing mechanisms, raw materials that in many cases belong to commodity polymers, acceptable properties for many different applications etc. contributed to the popularity of these coatings in the market very soon after their appearance in the beginning of the 1950’s. At the same time, however, weaknesses such as high temperature of fusion, low pigmentation level, poor solvent resistance and bad adhesion on metal surfaces necessitating the use of a primer can be listed. These problems inherent to the thermoplastic powder coatings were successfully overcome later on by the thermosetting powders which very quickly took the largest part (90 %) of the market.

Despite the disadvantages, thermoplastic powder coatings can offer some distinguished properties. Some of them possess excellent solvent resistance (polyolefins), outstanding weathering resistance (polyvinylidene fluoride), exceptional wear resistance (polyamides), a relatively good price/performance ratio (polyvinyl chloride) or high aesthetic appearance (polysters). These properties combined with the simplicity of the system, created a considerable market share for thermoplastic powder coatings.

Thermoplastic coatings are offered in a variety of performance classes (Figure 2.1). Besides the engineering and commodity polymers, which will be discussed in the following chapters, there are high performance polymers, e.g. PEEK (polyether ether ketones).

PEEK is a fully aromatic, semi-crystalline thermoplastic polymer with a maximum crystallinity of 48 %. It is a member of the class of polyarylether ketones (PAEK) high performance polymers. PEEK has a glass transition point of 143 °C and a melting range of ca. 340 °C. Characteristics of the polymer include a very high heat resistance and therefore service temperature, high rigidity, low water absorption, high hardness, good strength, low sliding friction, excellent chemical and hydrolysis resistance, low flammability, very low emission of smoke and toxic fumes during burning and its good electrical characteristics. PEEK offers one of the highest resistances against radiation among polymers.

Due to its high price PEEK is normally only used in applications where special properties are needed. Examples include valves, cable insulation, bearings, pump parts and sealings. Evonik Industries offers industrial grade PEEK under the trade name “Vestakeep”.

Figure 2.1: Performance/cost ratio of thermoplastics

source: Evonik Industries
2.1 **Vinyl powder coatings**

Two binders are used for the manufacture of the so-called vinyl powder coatings; polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF). On the basis of their polymer nature both powder coatings can be included in the same group, although they differ considerably in their performance. While PVC powder coatings are predominantly intended for indoor application because of their limited outdoor durability, PVDF powder coatings are among the best coating systems with respect to their weathering resistance.

Vinyl polymers belong to a group of resins having a vinyl radical as the basic structural unit. Polyvinyl chloride and copolymers of vinyl chloride are the most significant members of this group being among the first thermoplastics to be applied by powder techniques.

### 2.1.1 PVC powder coatings

Polyvinyl chloride powder coatings were introduced on the market in the time when the thermosetting powder coatings were in very early stages of development. PVC based coatings offered many advantages over the other thermoplastic materials available as binders for coating production. These coatings have very good resistance to many solvents, which is a rather poor characteristic of the thermoplasts, combined with resistance towards water and acids. They have excellent impact resistance, salt spray resistance, food staining resistance, and good dielectric strength for electrical applications.

Polyvinyl chloride (–CH₂–CHCl–)ₙ is one of the cheapest polymers produced by the industry on a large scale. Its basic properties include chemical and corrosion resistance, good physical strength and good electrical insulation. Polyvinyl chloride (PVC) is by nature a brittle polymer, but the flexibility of the material can be easily adjusted by using an appropriate amount of a suitable plasticizer.

Polymerization of vinyl chloride into PVC homopolymer or its co-polymerization with different co-monomers is carried out by a free radical mechanism. Most PVC resins are produced by emulsion or suspension polymerization of vinyl chloride in an aqueous system containing an emulsifying agent or suspension stabilizer. However, bulk and solution polymerization processes are also carried out on an industrial scale.

**Emulsion polymerization** of vinyl chloride can be performed in both a batch and continuous way. The reaction temperature is maintained between 40 and 50 °C by cooling the reactor in order to remove the heat developing during the polymerization. The reaction medium is de-ionized water containing enough proper surfactant to obtain a stable emulsion. The initiators used are peroxides soluble in water, such as hydrogen peroxide or different persulphates. Since the monomer itself is a gas at room temperature, the polymerization is performed under pressure in autoclaves. The pressure in the reactor falls as the polymerization proceeds. After reaching conversion of ca. 90 %, the content of the reactor is discharged and the unpolymerized vinyl chloride is recovered.

**Suspension polymerization** of vinyl chloride is an important process in the commercial manufacture of PVC. In principle it is a batch process, although attempts have been made to develop a continuous technique for suspension polymerization of PVC. The polymerization is carried out by first charging to the reactor the required amount of de-ionized water and adjusting the pH depending on the suspending agent used and then the dispersing agent and the initiator. The monomer is charged after sealing the reactor and evacuating the oxygen. The polymerization reaction is carried out under pressure at 40 to 60 °C, controlling the temperature by appropriate cooling of the reaction mass. Although a great amount of
research has been done in this area, it is interesting to note that the compositions of the reaction mass do not differ substantially from those used in the very early days of development of suspension PVC. The differences are mainly limited to the choice of the suspending agent, which is in most cases polyvinyl alcohol obtained by saponification of polyvinyl acetate, gelatin, methyl cellulose and copolymers of vinyl acetate with maleic anhydride. The initiator is water insoluble peroxide, such as lauril peroxide, or azobisisobutyronitrile.

The type of suspending agent plays a very important role in obtaining primary particles with high porosity. Gelatin normally produces glassy spherical particles which have poor plasticizer absorption characteristics, whereas polyvinyl alcohol gives particles of a porous nature which readily absorb plasticizers to give dry powder blends. Thus, a patent of Air Products and Chemicals, Inc. discloses a process for suspension polymerization of vinyl chloride giving a polymer specially suitable for production of powder coatings. The use of an excessive amount of secondary suspending agent causes two effects necessary for the critical powder coating application. Firstly, it reduces the size of the primary particles within the polyvinyl chloride grain, thus raising the surface to volume ratio and allowing plastication of the primary particles by the plasticizer. Secondly, very high porosity is gained, allowing complete and uniform plasticization of the resin grain in its entirety.

Solution polymerization of vinyl chloride is almost exclusively used for manufacturing copolymers containing vinyl acetate. The co-monomers are dissolved in a suitable solvent such as cyclohexane or n-butane, and the polymerization is carried out at 40 to 60 °C catalyzed by a free radical initiator which is soluble in the reaction mass. The copolymer begins to precipitate after a certain molecular mass is reached, which depends on the co-monomers’ ratio, polymerization temperature and type of solvent. The last step of the process includes filtering of the final product and then washing to remove the residual diluent and any traces of organic peroxide which would have a detrimental effect on the heat stability.

The bulk polymerization of vinyl chloride has been developed by Pechiney-St. Gobain, and plays an important role in the commercial production of PVC. Although bulk polymerization is associated with a homogeneous system, this is not the case with the bulk polymerization of vinyl chloride; namely, at very early stage of the reaction the polymer formed precipitates from the reaction medium in a form of insoluble material dispersed in the monomer. The system is therefore heterogeneous for a significant portion of the whole conversion. Since the polymer precipitates from the monomer, and there are no solvents present in the system, the concentration of the monomer available for polymerization remain constant with time. Therefore, at constant temperature the average molecular weight of the polymer obtained is apparently independent of the monomer conversion.

Bulk polymerization of vinyl chloride is performed in variants of the original Pechiney two-stage process. Vinyl chloride containing initiator is charged in a reactor and the polymerization is carried out at 50 to 60°C. Already at 1 % conversion the polymer begins to precipitate. After reaching conversion of about 10 % the entire content of the reactor is discharged in an autoclave where a further quantity of vinyl chloride is added. When the conversion is at about 20 % the material is in the form of a wet powder; at 40 % conversion the residual monomer is completely absorbed by the polymer and the mass takes on the form of a dry powder. The design of the reactor permits further polymerization which usually proceeds up to 90 % conversion. The residual monomer is then removed under vacuum and the polymer is discharged and sieved. Polymer particles with sizes larger than desired undergo additional grinding and sieving.

Polyvinyl chloride is an amorphous polymer containing very small amounts of imperfect crystallites. The average molecular weights for the most commercial PVC resins are in the range 50,000 to 120,000. Better physical properties are obtained by PVC having a high molec-
For applications in powder coatings, PVC resins with low molecular weight are more suitable because of lower melt viscosity and lower softening temperatures. Although different glass transition temperatures ranging from 68 to 105 °C are reported, depending on the method of polymerization and especially the temperature at which the polymerization is carried out, the normal commercial grades of PVC have $T_g$ of between 80 and 85 °C.

Figure 2.2 represents the differential thermal analysis curve of polyvinyl chloride. Five major regions of different thermal behavior can be noticed above room temperature. Matlack and Metzger[2] and Smith and Koleske[3] assign the glass transition temperature to the change of the slope at point A. The endothermic effect between 165 and 210 °C is a result of the melting of the crystallites present in the polymer. At 250 °C they define the point C as a region of oxidative attack, while at 300 °C (point D) the dehydrohalogenation takes place with evolving gaseous hydrogen chloride. Finally, at about 450 °C (point E) the endotherm is attributed to the occurrence of depolymerization.

Polyvinyl chloride is soluble in a wide range of organic solvents. The best solvents for PVC are tetrahydrofuran and cyclohexanone, but it is also easily solubilized by other ketones, halogenated hydrocarbons and nitrated aromatic solvents. However, from the standpoint of a powder coating producer it is important that PVC polymers are not soluble in alcohols and aliphatic hydrocarbons, and powder coatings having PVC as a binder possess considerable solvent resistance with respect to the most common solvents used in the industry.

The performance characteristics of the vinyl powder coatings have been compared by Christensen and are summarized in Table 2.1[4]. Comparisons of this type are always discussible. In this case, the outdoor durability of the vinyl polymers should be reconsidered, keeping in mind new developments particularly those of polyester thermosetting coatings. The table, however, gives a good indication of the characteristics of the vinyl powders with respect to the other thermoplastic materials.

The main problems of PVC powder coatings are related to the stability of the binder during processing, and also its brittle nature. These weak points were successfully overcome.
due to the enormous amount of work that was done on stabilization and plasticization of polyvinyl chloride. The result was development of a number of heat stabilizers, plasticizers and lubricants permitting problem-free hot compounding of the vinyl resins.

Because it is a rigid material not having sufficient flexibility polyvinyl chloride as such can not be used for powder coating purposes. In fact, only in a few applications can PVC be used without the addition of plasticizers. A wide range of high boiling materials has been developed for plasticization of PVC, such as esters of phthalic acid, phosphoric acid and aliphatic diacids. Liquid polymers or oligomers with relatively low glass transition temperatures are also used for the same purpose.

Phthalate esters are the cheapest plasticizers for PVC, proving to be very satisfactory over all properties. Di-2-ethylhexyl phthalate and diisooctyl phthalate have been the most widely used, offering a good price/performance ratio. But recently diisononyl phthalate gained more and more attention and market share due to a lower migration rate. It is also characterized with better oxidation stability and low-temperature flexibility.

Phosphate esters are used to obtain PVC products with self-extinguishing properties. Trixylyl phosphate is the most widely used material among the great variety of phosphate esters. The same self-extinguishing effect is obtained by the use of chlorinated paraffins. They in general cannot completely replace the so-called primary plasticizers of phthalate or phospate type, but they are quite competitive for price reasons. The common chlorinated paraffins used for plasticizing PVC have 42 to 56 % chlorine content and a chain length of C15 to C25.

Linear polyesters produced by esterification of dibasic acids with dibasic alcohols are plasticizers that provide good solvent resistance. They are especially suitable for PVC coatings in contact with hydrocarbon fuels or other organic solvents. However, polyvinyl chloride plasticized with polyesters exhibits relatively poor low-temperature flexibility.

The addition of the plasticizer to PVC improves the flexibility and the impact resistance of the polymer, but at the same time reduces the tensile strength, modulus and hardness of the plasticized material. The desired balance between hardness and flexibility can be achieved by careful choice of the type and amount of plasticizer. Although many efforts have been made to predict the behavior of the plasticized system by systematic approaches to this problem, the desired set of properties is usually achieved by making a series of formulations.

The curve representing modulus-temperature behavior of externally plasticized PVC with dioctyl phthalate (DOP) exhibits a typical drop of the modulus at the glass transition temperature at 80 to 90 °C with the rubbery plateau region afterwards in the non-plasticized PVC (Figure 2.3). A further increase of the temperature leads to melting of the crystallites, resulting in an additional drop of the modulus. The addition of DOP shifts the rubbery plateau to lower temperatures, but at the same time decreases the modulus, in this way affecting the hardness of the film.

The type and amount of added plasticizer must be determined in a way that will result not only in a good compromise between flexibility, impact resistance and hardness, but also in a way that will not affect the powder storage stability. Due to a concern over plasticizer leaching into food the market share of PVC has decreased, in particular in the western hemisphere.

Polyvinyl chloride that exhibits good mechanical properties has a molecular weight above 40,000. In pigmented systems, due to such a high molecular weight, there is a considerably more pronounced increase of the melt viscosity compared to the thermosetting binders. The
melt viscosity of PVC pigmented with TiO₂ shows an asymptotic increase at concentrations of the pigment between 15 and 25 % (by weight). This is almost four times lower than the concentration of the alkyd resins [3].

High melt viscosity of the pigmented PVC powder coatings is one of the reasons for their application in thick films in order to obtain good flow. Very often the low price of PVC powder coatings is compensated by the thick film application, losing in this way the advantage of having cheap and good quality protection. Smith and Koleske have suggested, that for film thickness below 50 µm, the melt viscosity during cure should be in the range between 50 and 500 Pa · s [3]. This corresponds to a weight averaged molecular mass of between 20,000 and 40,000 (Mn = 10,000 to 20,000), which is 2 to 4 times lower in value than the commonly used molecular masses.

PVC powder coating with a proper formulation should always contain a suitable stabilizer. An enormous amount of work has been done to elucidate the mechanism of thermal degradation of polyvinyl chloride. It is beyond the scope of this book to go into detail about the degradation phenomena of PVC. The overall reaction of decomposition involving hydrogen chloride will be presented simply as an illustration to help explain the role of the stabilizers:

\[
\text{Equation 2.1} \quad \text{Cl} + \rightarrow \text{+ HCl}
\]

The common property of all materials used for stabilization of polyvinyl chloride is the ability to react with hydrogen chloride. It seems rather strange that the stabilizer reacts with the product of degradation, i.e. it is active after the degradation has happened. Therefore, it can be assumed that the stabilizer decreases the rate of degradation, lowering the concentration of hydrogen chloride that may act as a catalyst for the degradation process. This can be accepted for some simple stabilizers such as the metal stearates. The experiments with labeled stabilizers of a metal soap nature or dialkyl tin dicarboxylates showed, however, that the soap or carboxylate moieties are retained to a greater extent than the metal or the alkyl groups. This indicates that the stabilizer is involved in some coordinate complex with the polymer chain, and that its action is not limited to a simple scavenging action of the evolved hydrogen chloride only.

A wide variety of materials has been developed for thermal stabilization of PVC. Such materials include mixed salts of calcium and zinc with rather inferior stabilizing properties, barium-cadmium soaps, lead sulfates, tin mercaptides, dibutyltin derivatives, di(n-octyl) tin maleate, amino crotonic esters, epoxy compounds, etc., though lead- and cadmium compounds are now forbidden in many countries for their toxicity.

A typical vinyl powder coating formulation containing a plasticizer and stabilizer is given in Table 2.2 [5].
Additives known as lubricants are often used in the powder coating formulation. They influence both the behavior during processing and the properties of the finished product. The primary requirements of the lubricants are to improve the flow properties of the fused compound, and to help the movement of the material through the extruder during the production of the powder coating by lubricating the interface between the PVC and the metal surface.

Two grades of lubricants are usually used for this purpose. The internal types which are compatible with PVC reduce the melt viscosity of the compound, improve the flow properties and reduce the friction in the processing equipment. The external lubricants which are not compatible with PVC act in this case only as a lubricating layer on the surface of the PVC where it comes into contact with the metal surface of the processing equipment.

Representatives of internal lubricants are long-chain fatty acids, calcium stearate, alkylated fatty acids and long-chain alkyl amines. External lubricants include fatty acid esters, high molecular weight alcohols, synthetic waxes, and low-molecular weight polyethylene.

PVC powder coatings applied by the fluidized bed method have been the most widely used materials for coating wire goods in thick layers. In this application they offer a good compromise between price and performance. They are characterized by uniformity of the coating, no sagging and good edge coverage. The usual thickness of the PVC powder coatings applied by the fluidized bed method is between 200 and 400 µm. To achieve good uniformity of the coating in thinner layers, the electrostatic spray technique is required.

Typical products coated with PVC powders are appliances and dishwasher racks. In the latter case, PVC coated materials can withstand the normal testing conditions of total vapor and water immersion at 80 to 100 °C without blistering. Detergent resistance and resistance to food stains are excellent. This is combined with the important characteristic of allowing the water to run off from the coated products. PVC powder coatings provide another important characteristic to dish racks by acting as sound dampers, thus preventing the development of noise during filling or discharging of the racks. Chemical and detergent resistance makes them suitable for protection of dishwasher tubes.

The non-toxic nature of the PVC powder coatings allows them to be used for refrigerator racks, freezers and shelves. The stain resistance and low odor of PVC powder coatings are appreciated characteristics in coatings for shelves made of wire, expanded metal or sheets. For the same reasons they are used as metal furniture coatings.

Good dielectric properties of PVC powder coatings are among the pre-requisites they fulfill for application in the electric and electronic industries. The soft touch feeling makes them suitable for covering various types of handles, automotive seat belt anchors, bus bars, tools etc.

Outdoor durability is not a strong point of PVC powder coatings. The main reason is the sensitivity of the binder to the ultraviolet spectrum below 350 nm. The development of effective UV stabilizers has opened up new possibilities for outdoor use of PVC powders.

### Table 2.2: Vinyl powder coating formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakelite vinyl resin QYNJ (1)</td>
<td>100.3</td>
</tr>
<tr>
<td>Bakelite vinyl resin QYJV (1)</td>
<td>9.3</td>
</tr>
<tr>
<td>Flexol plasticizer EP-8 (1)</td>
<td>6.0</td>
</tr>
<tr>
<td>Flexol plasticizer 10-10 (1)</td>
<td>36.0</td>
</tr>
<tr>
<td>Mark C (2)</td>
<td>2.0</td>
</tr>
<tr>
<td>Thermolite 31, PVC stabilizer (3)</td>
<td>6.0</td>
</tr>
<tr>
<td>TiO₂-rutile</td>
<td>20.0</td>
</tr>
</tbody>
</table>

(1) Union Carbide Corp.; (2) Argus Chemical Corp.; (3) M&T Chemicals, Inc.

Source: Communication Channels Inc.
A large market for **exterior use** of PVC powders developed in USA includes the electrical transformer, whose manufacturers give a 20 year guarantee for their products coated with PVC powder \[^6\]. The successful development of thermosetting powder coatings specially designed for outdoor application is certainly a big obstacle for PVC powders to compete in the market for outdoor coatings.

### 2.1.2 Fluor based powder coatings

The best representative of vinyl polymers exhibiting **outdoor durability** is polyvinylidene fluoride (PVDF). Powder coatings based on PVDF have the highest resistance to degradation on outdoor exposure, very good abrasion resistance, excellent chemical resistance, very low surface friction, ice release properties, and very low fluid absorption.

PVDF is produced by free radical polymerization of vinylidene fluoride, using peroxides as initiators, or coordination catalysts of the Ziegler-Natta type. Different patents describe various methods for polymerization of vinylidene fluoride including emulsion, suspension or solution polymerization \[^7\]–[^12]\. The structure in the repeating unit of polyvinylidene fluoride is \(-\text{CH}_2\text{–CF}_2\text{–}\). Hydrogen and fluorine atoms are spatially symmetrical, which optimizes cross-bonding forces between polymer molecules. Polyvinylidene fluoride is a **crystalline polymer** with a melting point between 158 and 197 °C. It exists in two different crystalline forms: the so-called alpha form has a **trans-gauche-trans-gauche** conformation, while the other beta form possesses a planar zigzag conformation \[^13]\. The polymorphism of PVDF is the reason why the melting point, which is in a considerably broad temperature range, is not well defined. The relatively high melting point allows PVDF to be used permanently in a relatively broad temperature range from -40 up to +150 °C which corresponds with its glass transition temperature and the lower border of the melting range.

Polyvinylidene fluoride is characterized by a high mechanical and impact strength and very good abrasion resistance combined with excellent flexibility and hardness. Even better flexibility and elongation is achieved by copolymerizing it with hexafluoropropylene \[^14]\. Carbon steel coated with this copolymer could be a cost-effective alternative to stainless steel.

PVDF homopolymer is resistant to attacks by most corrosive chemicals such as acids, alcalis, strong oxidizing agents, etc. It is also not soluble in the common solvents used in the coating industry. Some highly polar solvents can only soften the surface of the polyvinylidene films temporarily. The only chemicals that can damage the surface of the PVDF films are fumic sulfuric acid and strong primary amines. PVDF complies with the requirements of the Food and Drug Administration (FDA) for materials that can be used in the food processing industry and allowed to come in direct contact with food.

PVDF powder coatings have been recognized as materials with **exceptional properties** such as low friction and abrasion, oil and water repellency, extremely good outdoor durability, excellent flexibility, corrosion and chalking resistance, resistance to chemicals and aggressive industrial atmospheres rich in SO\(_2\). They are very easy to maintain because of extremely low dirt pick-up properties. These unique properties are due to the small bond polarization of the fluorine-carbon bond, which is responsible for the low surface energy of the PVDF used as a binder in these coatings. The very high bond energy of the carbon-fluorine bond (477 kJ/mol) provides exceptional weathering resistance \[^15\], \[^16\]. PVDF can be used as a sole binder in the manufacture of powder coatings, especially when high weathering resistance is required, although this is not a common case in practice. The main reasons include the high melt viscosity resulting in the formation of pinholes during thin film applications, rather poor adhesion to metal substrates, and the relatively **high price**. 3M filed a patent application \[^17]\ describing the addition of hydroxyl or amine functionalized...
Thermoplastic powder coatings

Aromatic compounds like fluorophenol or 2-naphtol to fluoropolymers to enhance adhesion to metals and ceramics. Daikin Industries claimed that adhesion as good as on chromium phosphate primers is achieved by the combination of amido and/or imido containing fluoro resins.

In order to improve the melt flow properties, adhesion and aesthetic appearance of the powder coatings, acrylic resins are usually blended with PVDF. It is common that the binder for PVDF powder coatings contains 30% acrylic resins. Higher amounts of acrylic resin decrease the weathering resistance of the coatings, although it still remains superior to other manufactured organic coating materials known so far.

Alternating copolymers of tetrafluoroethylene and ethylene are claimed to have excellent mechanical strength and processability making them suitable for chemical plant equipment, reactors, vessels and pipes.

The results of a study of the weathering resistance of PVDF coatings containing 25 to 40% acrylic resin baked at 300 °C are presented in Figure 2.4. Similar results with respect to accelerated weathering in OUV apparatus are obtained by PVDF powder coatings containing 30% acrylic resin, baked for 10 minutes at 230 °C (Figure 2.5).

PVDF powder coatings have low gloss in the range of 30 ± 5% (at 60°). This is certainly a restriction for a whole range of application of PVDF powder coatings for decorative purposes.

The process of production of PVDF powder coatings does not differ from that of the other powder coatings. It consists of extrusion of the resins and pigment premix in a single or twin screw extruder followed by granulation and drying of the granulate. The next step is cryogenic grinding and sieving in order to obtain powder particles below 50 µm. An alternative method has been described in a Japanese patent. Fluor containing polymers are dissolved in isophorone at 200 °C, spray-dried to spherical particles, applied electrostatically on stainless steel and heated at 300 °C to give a pinhole free coating.

The very low surface energy of PVDF, which provides low dirt pick-up properties to the coating, at the same time, causes difficulties concerning adhesion to the substrate. This, in general a weak point of thermoplastic powder coatings, is even more emphasized in the case of PVDF powders. As already mentioned, the blends with acrylic resins improve adhesion, but even in this case, direct application of the PVDF powder coatings to a metal substrate is not recommended. For good adhesion, PVDF powder coatings are applied over an epoxy stoving primer. Systems based on polyurethane primer with a PVDF top coating are also reported. A Chinese publication recommends an addition of fluoroethylene-propylene-polyphenylene sulphide mixtures for enhanced adhesion on metals.

The problem of bad adhesion can be overcome in the way described in the US patent from 1974 where a two-coat system based on polyvinylidene fluoride is used. The first primer coating is produced by physical mixing of polyvinylidene fluoride of a particle size from a 60 to 200 mesh and silica sand of a particle size from a 150 to 325 mesh. The adhesion of the coating was tested by exposure to steam at 100 °C. The time before the occurrence...
of blisters, taken as the relevant parameter for estimation of the adhesion properties of the system, ranged from 7 hours in the case of the primer containing no silica sand to more than 480 hours for the one having a PVDF/silica ratio of 100/40 or more. Similar results were obtained with a primer in which graphite of the same particle size was used instead of silica sand [23].

Recently Arkema published a patent [26] in which maleic anhydride was grafted on PVDF by means of $\gamma$-radiation. These modified PVDF resins show a significant improvement in adhesion on untreated metal substrates like aluminum.

Although for the coil coatings based on PVDF as a binder a 20 year guarantee is normally given [15, 23, 27], for PVDF powder coatings containing 30 % acrylic resins, a 10 year guarantee for a maximum of 50 % loss of the initial gloss has been granted [20].

PVDF powder coatings are mainly used as architectural coatings for monumental-type structures. Architectural panels for roofing and wall claddings, and aluminum extrusion window frames are the main surfaces on which PVDF powder coatings have been applied.

### 2.2 Polyolefinic based powder coatings

The discovery of the new coordination catalysts for polymerization of olefins in the first half of the 1950’s resulted in the development of a new class of polyolefins. This invention has not only made a big commercial impact, but has also contributed very much to the development of polymer science.

By the use of coordination catalysts, or the so-called Ziegler-Natta catalysts after the names of the inventors, polypropylene and low pressure polyethylene are produced on an industrial scale, being two of the most important thermoplastic polymers of this century. They are the main representatives of the polyolefins used in the manufacture of powder coatings. Being non polar, high molecular weight crystalline polymers, with carbon-carbon bonds in the polymer backbone, they possess a unique balance of toughness, chemical and solvent resistance. It is obvious that such materials could be of great inter-

![Figure 2.5: Accelerated weathering (QUV) of PVDF white and brown coatings compared with polyester powder coatings](source: Technology Communicative Markt BV)

<table>
<thead>
<tr>
<th>Property</th>
<th>High pressure process</th>
<th>Medium pressure process</th>
<th>Ziegler process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>65 %</td>
<td>95 %</td>
<td>85 %</td>
</tr>
<tr>
<td>Relative rigidity</td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Softening temperature</td>
<td>104 °C</td>
<td>127 °C</td>
<td>124 °C</td>
</tr>
<tr>
<td>Tensile strength [bar]</td>
<td>138</td>
<td>380</td>
<td>241</td>
</tr>
<tr>
<td>Elongation [%]</td>
<td>500</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Relative impact strength</td>
<td>10</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>0.92</td>
<td>0.96</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*Table 2.3: Typical properties of polyethylene obtained by the three basic processes [30]*

*source: John Wiley & Sons, Inc.*
Thermoplastic powder coatings

est when used as binders for protective coatings. However, their insolubility in the solvents commonly used by the paint industry restricted their application to the powder coatings only. In fact, one of the first powder coatings which were used in a fluidized bed application at the beginning of the 1950’s, was based on powdered polyethylene [28].

The empirical formula of polyethylene \(-\text{(CH}_2\text{-CH}_2\text{)}_n\text{-}\) is rather simple and does not indicate the many implicit structural possibilities that can exist, offering products with different properties and uses. The molecular weight of polyethylene and molecular weight distribution, the amount and length of side chains that depend on the manufacturing conditions, together with different degree of crystallinity are parameters that influence to a great extent the properties of the polymer. The crystallinity of polyethylene in particular, directly reflects the degree of packing of polymer chains and thus the density of the material and is an important parameter distinguishing several classes of commercial products in the market. According to the ASTM classification, commercial grades of polyethylenes are grouped into four types based upon densities regardless of the molecular weight or molecular weight distribution:

<table>
<thead>
<tr>
<th>Type</th>
<th>Density ([\text{g/cm}^3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.910 to 0.925</td>
</tr>
<tr>
<td>II</td>
<td>0.926 to 0.940</td>
</tr>
<tr>
<td>III</td>
<td>0.941 to 0.959</td>
</tr>
<tr>
<td>IV</td>
<td>0.960 and higher</td>
</tr>
</tbody>
</table>

When the density or crystallinity of polyethylene is reduced, then the impact resistance, cold flow, tackiness (blocking), clarity and permeability increase. On the other hand, a reduction in density produces a decrease in stiffness, tensile strength, hardness, abrasion resistance, brittleness temperature, softening point, fusion temperature, chemical resistance and shrinkage.

Both, low and high density grades polyethylene are successfully used for the manufacture of powder coatings. The high density grade is suitable for industrial application, while the low density is used for domestic applications [29]. The first process with a commercial potential of polymerizing ethylene under high pressure and temperature was discovered in the laboratories of Imperial Chemical Industries, Ltd. in 1933. Polyethylene produced in this way (temperatures of 100 to 300 °C and pressures above 1000 bar) has a high molecular weight, broad molecular weight distribution, a high degree of branching, moderate crystallinity and low density.

By the discovery of Ziegler in 1953 polyethylene was produced in an astonishingly simple process at atmospheric pressure and almost room temperature by using alkyl aluminum compounds combined with titanium tetrachloride as catalyst. This was an outstanding event not only from the technological point of view, but also because it offered polymer that was highly oriented with a high degree of crystallinity, almost without side chains, and properties that differed very much from those obtained by the high pressure process.

Another method of production of polyethylene was developed in USA about the time of Ziegler’s discovery, and employed medium pressure and temperature during polymerization in the presence of metal oxides as catalysts. These processing conditions lie in between high pressure polymerization and the process of Ziegler.

Table 2.3 presents the basic differences in the properties of polyethylene polymers obtained by these three different methods [30]. Other important differences from the standpoint of the powder coating chemist are presented in Table 2.4 [30].

The other representative of polyolefins that is used as a binder for powder coatings, polypropylene, can be produced by a wide variety of catalysts, including cationic, anionic and...
free radicals. The technique for polymerizing polyethylene under high pressure has been unsuccessful for polypropylene. The explanation is that polypropylene radicals tend to chain transfer to \(C_3H_6\) giving the unreactive allyl radical. Therefore, the free radical polymerization of propylene has almost no commercial importance.

The polymerization process catalyzed by cationic catalysts of Friedel-Crafts type results in amorphous polypropylene of low molecular weight. There is a typical drawback of the polypropylene obtained in this way, which restrict the application of the polymer in the powder coating field; namely, the polymer chains obtained by cationic polymerization are without structural order. As a consequence, crystalline polymers can not be made by this route.

The production of polypropylene with properties useful for most modern applications became possible with the discovery of the Ziegler-Natta catalysts. The polymerization of propylene by the anionic coordination mechanism produces a stereo regular crystalline polymer with a melting point high enough from a practical standpoint. As a consequence, crystalline polymers can not be made by this route.

Three types of polypropylene can be distinguished with respect to the stereo regularity of the chains. Atactic polypropylene without a regular structure and obtained by cationic polymerization is an amorphous, soft and tacky material with little or no physical strength. On the other hand, isotactic and syndiotactic polypropylenes are obtained by anionic polymerization. These structures are schematically presented below:

\[
\text{Equation 2.2}
\]

The ordered structures of the syndiotactic and isotactic polypropylene allow a great degree of crystallinity resulting in a polymer with high physical strength, solvent resistance and chemical resistance.

The anionic polymerization of propylene mainly gives the isotactic type of polymer. This is one of the lightest commercial plastics with a density of only 0.9 g/cm\(^3\). The melting point is in a range from 165 to 170 °C for the commercial grades, while the melting point of 100 % isotactic polypropylene is 183 °C.
Syndiotactic polypropylene is not produced on a commercial scale. Its melting point is about 20 °C lower than that of the isotactic type, and it is more soluble in ether and hydrocarbon solvents.

The same catalysts used for production of high density polyethylene at atmospheric pressure are suitable for polymerization of polypropylene. The catalytic system usually includes titanium chloride, an aluminum compound, preferably trialkyl aluminum or aluminum chloride, and optionally a Lewis base or other modifier.

**Polypropylene** has a number of desirable properties that make it a versatile material for production of powder coatings. It possesses good surface hardness and is scratch and abrasion resistant. It is essentially unaffected by most chemicals and possesses excellent solvent resistance. It is somewhat more brittle than polyethylene at normal temperature, which is caused by the relatively high glass transition temperature ranging between 25 and 35 °C depending on the degree of crystallinity. The brittleness of the commercial grades and impact resistance are markedly improved by copolymerization with other olefins. Considerable amounts of polypropylene are sold as copolymer containing 2 to 5 % of ethylene. The resulting polymer has increased flexibility, toughness, impact resistance and clarity, and somewhat lower melting point.

The fact that the fragility of polyethylene and polypropylene is increased by cooling with liquid nitrogen or by soaking with alcohol before grinding is used as the basis for several techniques to make fine powders. Also some polymerization processes yield polyethylene directly as fine powder. High-pressure polyethylene, however, is produced as a solid resin and must be ground to produce powder.

Because of the carbon-carbon bonds in the molecular chains, polyethylene and polypropylene powder coatings exhibit very good chemical resistance. Due to the nonpolar paraffinic nature of the binder they have a reputation for coatings with excellent solvent resistance. Therefore, a very **important application** field for polyethylene and polypropylene powder coatings is the protection of chemical containers, pipes and pipelines for keeping and transporting different chemicals and solvents.

Being inert materials, polyolefins have **poor adhesion to metal** or other substrates. Therefore, before polyethylene and polypropylene powder coatings can be used successfully, the surface to be coated must first be primed or adhesion promoters must be added to the powder coating to improve adhesion. A family of adhesion promoting polymers, called “Hercoprime”, has been developed, which, when blended with polyolefins, and specially with polypropylene, give a one-coat system with good adhesion \(^6\,\!\!^3\). These polymers are produced in the form of small particles whose size is of a range typical for powder coatings. Their density is similar to that of polypropylene, and they can be used by simple tumble blending with polypropylene powder coatings. For pigmented systems, a 15 % addition of these adhesion promoting resins provides good adhesion for most of the substrates. Clear propylene coatings need 5 to 10 % of primer promoter to exhibit satisfactory adhesion properties \(^3\). Different modifications of polyolefins have been tried in order to improve the adhesive properties. In some cases these are simple blend of polyethylene or polypropylene with polymers containing acid groups as adhesion promoters. A Dainippon patent \(^3\) describes a modified polyolefin composition prepared from 60 to 97 part of polyolefin, and 3 to 40 parts of copolymer based on 20 to 60 % acid monomers, 40 to 80 % styrene and 0 to 40 % alkylmethacrylates. It is claimed that the powder coating possesses excellent adhesiveness, coatability and color stability. In examples of another patent referring to improved adhesion of polyolefin powder coatings \(^4\,\!\!^4\), 0.05 to 40 parts of a polypropylene modified product containing 15 to 30 % by weight grafted maleic anhydride and 99.5 to 60 parts of polyolefins...
Polyolefinic based powder coatings

are used as a binder composition for polyolefin powders. Excellent adhesion of the coating is combined with excellent mechanical properties.

At the PCE 2002 Congress in Nuremberg, Plascoat \cite{35} also came with a thermoplastic coating powder, based on an “alloy” of acid modified polyolefins. They claim their powder has excellent adhesion to the metal substrate, without the need of a primer. The material also provides good abrasion and impact resistance and is resistant to stress cracking and adverse weather conditions.

A powder composition with improved adhesion properties is obtained by physical mixing of polyethylene powder with powder of copolymer comprising 60 to 95 % of ethylene and 5 to 40 % of glycidyl methacrylate \cite{36}. The coating is applied in a fluidized bed on a preheated surface at 300 °C followed by postcuring at 200 °C for 20 minutes. It is claimed that the adhesion properties of this coating are much improved in comparison with pure polyethylene powder. A Chinese research group filed a patent application \cite{37} describing the beneficial effect of silane modified nano-silica for the adhesion and corrosion resistance of polyethylene coated steel pipes.

Ethylene vinyl alcohol copolymers are described \cite{38} to be highly resistant against hydrocarbons and organic solvents. In addition they show outstanding oxygen barrier properties which make them suitable for chemical packaging, fuel tanks and protective clothing.

**Polyethylene** powder coatings are even more problematic with respect to adhesion properties than polypropylene powders. Priming of the surface is usually necessary prior to application of the polyethylene powder coating, since the adhesion promoting resins do not perform as well as in case of polypropylene. A patent assigned to Hoechst describes a two-step method for heavy duty protection of pipelines for the transport of oil \cite{39, 40}. In the first step, a bisphenol A epoxy resin with amino hardener is sprayed over preheated metal pipe at 270 °C in a 100 µm thick layer. The still soft, highly viscous layer is coated with a powder coating consisting of 75 % polyethylene and 25 % copolymer of vinyl acetate-ethylene-acrylic acid-alkyl acrylate in a weight ratio of 3:76:1:20. The total thickness is very high (above 2 mm) providing extremely good mechanical protection. Pipes can be transported without damage over rocky ground, they are heat stable and they resist desert conditions.

Three-layer polyolefin pipe coatings have gained widespread international acceptance. The first layer is thermosetting epoxy powder or solventless liquid coating with a thickness between 60 and 100 µm. The intermediate polymer layer with a thickness between 250 and 400 µm is a polyethylene powder coating and is applied over the epoxy primer, followed by the third layer as a topcoat which is applied by extrusion with a coating thickness between 1.5 and 3.0 mm. These systems are well established in Europe, the Middle East and Asia, offering excellent corrosion resistance and interfacial properties of epoxy coatings, combined with excellent chemical, solvent and mechanical resistance of the thick polyethylene coatings. The Hajira-Bijaipur-Jagdispoor 2800 km long pipeline system in India is an example of one of the major operations to be coated with three-layer polyethylene coatings \cite{41}.

A one-step application procedure refers to a coating system that combines the excellent anticorrosive properties of zinc dust, adhesion of the epoxy powder coating and good solvent, chemical and weather resistance of the polyethylene powder coating \cite{42}. An epoxy powder coating comprising bisphenol A epoxy resin as the main binder, dicyandiamide as the hardener, barium sulfate and carbon black as the filler and pigment, catalytic amounts of amine accelerator and flow additive with particle size of 75 to 150 µm, is dry blended with clear polyethylene powder and zinc dust in the ratio of 70:30:5. Powder coating prepared in this way has been applied on steel panels using an electrostatic spray gun in a one-step operation. After curing for 3 minutes at 150 °C and raising the temperature at a linear rate
to 215 °C for 10 minutes, a flat finish is obtained with a clear polyethylene top coating and a zinc-rich bottom layer covered with an epoxy intermediate thick layer. The main proposed application is to coat the interior of underground oil or gas pipes. The zinc layer produces a galvanized finish on the interior of the pipe, while the epoxy part overlaying the zinc serves to protect the zinc from abrasion as well as providing an integral coating with high corrosion resistance. The polyethylene top coating is an electrically non-conducting layer, and thus prevents or minimizes electrolytic corrosion, providing at the same time excellent solvent resistance. The same coating technique is proposed for applications where the polyethylene top coating contributes in improving **exterior durability**, for example in coating automobile wheel rims.

**Kodokian** and fellow researchers [43] at DuPont describe a novel approach of reacting a thermoplastic ethylene copolymer with a solid bisphenol A epoxy, which provides the possibility of a new and tough corrosion resistant powder coating system, that is not readily available from pure thermoset powders. They use an ethylene copolymer with (meth)acrylic acid for reaction with the epoxy resin and catalyze it with 0.5 to 1 % TBPPb (tetrabromophosphonium bromide). They suggest end uses for these modified thermoplastic systems as automotive and industrial metal coatings and even as coatings for heat sensitive substrates.

Powder coatings based on polyolefin polymers have a **low aesthetic appearance**, and, therefore, are used mainly for protective rather than decorative purposes. For pigmentation, dry blending techniques with high shear mixers can be successfully used. This is not of course a suitable technique for highly decorative coatings, but in general, for protective polyolefin powder coatings, it seems to be a method that gives good compromise between processing costs and coating performances.

In the case of polypropylene powder coatings, high gloss can be obtained by water-quenching immediately after fusion. Because of the rapid cooling, the spherulite size of the crystalline polypropylene is smaller, resulting in a film with less surface roughness and imperfections combined with higher flexibility. Coatings with better aesthetic appearance can be obtained by using higher molecular weight polyolefins, since the crystallization rate considerably decreases due to the reduced polymer chain mobility in the melt.

Physical aging of high molecular weight polypropylene has in principle a less emphasized effect on decreasing impact strength. High molecular weight polypropylene powder coatings retain their initial impact strength over a six-month period after quenching, while lower molecular weight grades exhibit slight decreases with time.

Polyolefinic powder coatings are resistant to a variety of hostile environments. **Solvent resistance** at room temperature is excellent against all common solvents used in industry. However, at elevated temperatures, non-polar solvents, such as hydrocarbons and aromatics, will swell or in extreme cases dissolve the coating. Resistance against water, salt solutions, detergents, acids and bases is excellent. Only very strong oxidizing agents, such as nitric acid, will attack the coatings at room temperature.

Although polyolefinic powder coatings are not recommended for outdoor use where decorative purposes are requested, stabilized versions of polypropylene can be used for the manufacture of powder coatings with reasonable gloss retention when exposed to weathering conditions. The main use of polyethylene and polypropylene powders, however, remains in the field of **functional coatings** with excellent protective properties. Applications for these functional coatings include appliance parts, such as dishwasher racks, refrigerator racks, washer tubes, metal containers, drums, pipes, electrical applications and industrial equipment components [44]. Polyolefinic powder coatings comply with FDA regulations, and can be used for covering surfaces which come in direct contact with food products.