1 Thermoplastic Polymers Used in Textile Coatings

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1.1 Introduction

Polymer-coated textiles are flexible composite materials comprising the coat (the polymer) and the substrate (textile layer(s)) adhered together through a specific coating process to provide additional properties for the system. A military tent can be made of a material that combines Nylon fabric with a Neoprene coat, whereas a urethane-coated polyester cloth can be used to make the inflatable chutes installed at the emergency exits on aircrafts. Other examples include protective clothing for firemen, waterproof jackets, and seat upholstery for cars. In this context, there may be two or more layers in the polymer-coated textile system, at least one of which is a textile fabric and the other is the thin continuous polymeric layer (the coat). Combination of various properties of each layer determines the overall properties of the system. That is, the textile substrate contributes to the strength (tear and tensile), elongational and dimensional properties of the system in general, whereas the polymer coat helps to introduce resistance to penetration and impermeability (to liquids, gases and dust particles), as well as improve fabric abrasion. In certain special applications, the coat can also help to increase conductivity, to provide shielding from electromagnetic interference/radiofrequency interference (EMI/RFI) and to introduce antimicrobial properties. They can also help to modify the appearance for decorative purposes.

The layers (of the textile and the coating) are bonded to each other in situ by the adhesive properties of the layers leading to the ‘coated fabric’, or by the use of an added adhesive leading to the ‘laminated fabric’. In this book, the first group of systems is mainly considered.

The first step in the production of a coated textile fabric is ‘direct spreading’ of the (thickened liquid or paste) polymer in liquid form over the textile surface. The thickened liquid is allowed to evaporate, leaving the polymer on the fabric (if solvent-based) or allowed to transform into a coat (if plastisol- or dispersion-based); both of these processes are carried out in special ovens. During this process, appropriate
crosslinking (‘curing’) of the polymer coat is achieved to improve durability to abrasion and resistance to solvents (and water). This type of processing has the advantage of producing coats without mechanical or thermal stresses; however, it has the disadvantage of removal of large amounts of solvent or dispersion medium, which is energy-intensive.

The combination possibilities of the textile and coating are almost infinite, and are dependent upon final use. The polymer coat can be on one (or both) side(s) of the substrate (with identical or different types of polymers on each side), whereas the substrate can be a woven, knitted or even non-woven textile material.

Polymer-coated textiles have a very specific, important position in technical textiles and in everyday life due to their wide range of interesting applications. Some of these products are used in aerospace, automotive (e.g., airbags), chemical processing, electronic, geotextile, military, filtration and heating, venting and air conditioning applications. Other products are used in carpeting, protective clothing, fuel cells, or home furnishing applications. Examples of applications include inflatable boats, folding kayaks, gloves, snowshoes, tents and fuel tanks.

The overall properties of a polymer-coated textile are mainly dependent upon the:

- Characteristics of the textile substrate (with the exception of metallic, glass and inorganic fibre woven textiles, all other textile substrates are always polymeric).

- Characteristics of the coat applied (which is also a polymer).

- Coating/adhesion method(s) selected and employed [1] in which the adhesive used is polymeric in general.

Polymer-coated textiles can differ in material type. There are systems made from textiles of acetate/triacetate, acrylic/modacrylic, aramid, elastomeric, fluoropolymer, polyamide (PA), olefin, polyolefin, polyester, polyethylene (PE), Rayon, styrene-acrylonitrile, and polyvinyl chloride (PVC). Some coated fabrics are made of natural fibres such as cotton, wool, hemp, jute, linen (flax) or silk. Fibres of glass, fibreglass, E-glass, S-glass, rock wool, slag wool, ceramic, boron, carbon, graphite, silica, metallic fibres, and zirconia are also available.

Polymers play a dominating part in all of these systems for textiles and the coatings involved. Hence, a solid background and knowledge of polymer science and technology in addition to knowledge of textile technology and the principles of chemical engineering are prerequisites for the topic.
In the following section, a quick summary will be provided for polymers, whereas some basics of the textile substrate will be outlined in subsequent chapters.

### 1.1.1 Polymers and their Classification

A polymer is a large molecule (polymer chain) built up by the repetition of a small, simple chemical unit (‘repeat unit’), which is usually (or nearly equivalent) to the monomer, or starting material from which the polymer is formed [2].

The length (and size) of the polymer chain is characterised by its molecular weight, specified by the number of repeat units in the chain multiplied by the molecular weight of the repeat unit. To have polymers with minimum agreeable mechanical properties, it is essential to have polymers with molecular weights >10,000. This is because polymers with lower molecular weights are in the form of friable powders and cannot be put into a film. In fact, most high polymers used have molecular weights between 10,000-1,000,000.

Polymers can be synthetic (those produced synthetically (termed as being ‘man-made’)) or natural (produced by nature). There are >30,000 natural and synthetic polymers. Ninety percent are natural, and ~10% of them are synthetic.

Synthetic (man-made) polymers are mainly derived from petroleum, natural gas and coal as feedstocks. Annually, >150 million tons of synthetic polymers (about 20 kg per person) are produced worldwide.

Synthetic polymers can be subdivided into three main categories depending on their thermal responses:

- **Thermoplastics** consist of individual long-chain molecules that can be softened with temperature and hence are, in principle, ‘re-processable’.

- **Thermosets** are strong three-dimensional (3D) networks in which individual long-chain molecules are interconnected to each other by strong ‘primary’ covalent bonds (also termed ‘chemical crosslinks’). Thermosets are usually created in the final form of the product and can be broken down only at high temperatures. They are hard and glassy at room temperature (their glass transition temperature ($T_g$) values, if there are any, are much higher than ambient) and they cannot be softened by heat. Hence, they are not re-processable.

- **Rubbers** have looser 3D highly flexible networks. They are soft and elastic at room temperature. Between the chains, there are physical entanglements acting as ‘physical crosslinks’.
Advances in Polymer Coated Textiles

According to these definitions (chemically) crosslinked rubbers are considered to be ‘thermosets’.

Several thermoplastics and rubbers are widely used as the coating material. Textiles applied as substrates can be prepared from natural (e.g., cotton) and/or synthetic thermoplastic polymers.

Appropriate adhesion of the textile substrate to the polymer coat is very important in almost all cases, so special polymeric adhesives are also employed.

Further key information for these three main categories of polymers is provided next.

1.1.1.1 Thermoplastics

There are four main types of thermoplastics in common use: PE, polypropylene (PP), PVC and polystyrene. These are also referred to as ‘commodity thermoplastics’.

PE thermoplastics can be low-density (LDPE), high-density (HDPE) or linear low-density in addition to ultra high molecular weight, and medium molecular weight.

Commodity thermoplastics have low densities, ranging from 900–970 kg/m$^3$ (PE and PP) to 1400 kg/m$^3$ (PVC). This means that they have relatively low material costs per volume.

The second group of thermoplastics are engineering thermoplastics. They have better mechanical properties than commodity thermoplastics. Examples include polyethylene terephthalate, polybutylene terephthalate, PA (or Nylons), polycarbonate, polymethyl methacrylate (PMMA) and polyetheretherketone. They are characterised mainly by their strengths, with high stability performances in continuous use at temperatures >100 °C. Engineering thermoplastics are produced and used on a small scale and have prices higher than those for commodity thermoplastics.

The final group of thermoplastics is speciality plastics. They have specific properties (e.g., high heat resistance, exceptional mechanical properties). They are usually produced in limited amounts and are the most expensive. Polytetrafluoroethylene (PTFE; Teflon) is considered to be a speciality plastic with unique low-friction properties.

In terms of microstructures, thermoplastics can be amorphous glassy or a semi-crystalline solid. The amorphous thermoplastics are glassy up to a specific temperature (the $T_g$), above which they transform into a more rubbery structure without a distinct
melting point. Semi-crystalline thermoplastics are two-phase materials comprising an amorphous phase with the certain $T_g$ and a crystalline phase with a specific melting temperature ($T_m$).

In general, the size of the polymer chains (which characterises the average molecular weight) and the melting points are directly inter-related up to a certain point. That is, systems with shorter chain lengths melt at relatively low temperatures; the bigger the size of the chains the higher the melting point.

There is a similar hyperbolic relationship between $T_g$ and chain length up to a characteristic chain length. Usually, the $T_m$ and $T_g$ values of polymers are presented for systems with chain lengths above those ceiling values, which are characteristic of the polymer chains under consideration.

1.1.1.2 Thermosets

Almost all thermosets are hard, rigid and brittle, with high temperature and chemical resistances. They are usually used as matrices for reinforced composites. The crosslinking reaction (which occurs in the final stage of the product) is usually used to provide good adhesion with other polymers. Some thermosets such as epoxy, phenolics and polyester resins, are mainly used as the matrices for fibre-reinforced composites, whereas amino resins are mainly used for bonding chipboard.

If the number of branch points in a polymer system is progressively increased, long branched molecules with infinite ‘tree molecules’ are initially formed and ultimately a 3D network system is obtained. Formation of a single tree molecule (also called as the ‘gel point’) is when most of the polymer becomes non-soluble, and a swollen gel forms if a solvent is added to the system.

Thermosets and rubbers are examples of infinite 3D network molecules. In epoxy thermoset systems, there are two components: a prepolymer (of molecular weight ~1000–2000 with reactive epoxy groups at each end), and a multifunctional amine ‘hardener’. In the crosslinking reaction, the epoxy ring is opened and linked to four others of the prepolymer chain if they are used in stoichiometric quantities. For an epoxy thermoset, the upper limit for thermal degradation is typically at 145 °C.

Other thermoset systems usually produce less well-defined networks. For example, polyester thermoset systems are produced from a partially unsaturated linear polyester (of the step-growth polymerisation product of propylene glycol, phthalic anhydride and maleic anhydride). The number of C=C double bonds in the unsaturated linear polyester (hence the degree of crosslinking and $T_g$) are determined by the proportion
of maleic anhydride to phthalic anhydride used. In the curing (crosslinking) stage, these double bonds react with styrene to produce links of 1–3 styrene units.

The extent of the crosslinking reaction for thermosets increases the number of crosslinks and hence the $T_g$. The upper limit of the highest temperature for decomposition for any particular thermoset is characterised by the thermal resistances of the bonds involved.

### 1.1.1.3 Rubbers

Rubbers are crosslinked amorphous polymers and their $T_g$ is characteristically at or below 25 °C. In these systems, there are no rigid groups (such as phenyl rings) in the chain or as side groups, and no polar groups that can increase intermolecular forces.

Rubbers are dominated by commodity types, such as natural rubber (NR) and styrene-butadiene copolymer rubber, which are largely used for tyre production. In this and many other applications (e.g., conveyor belts, pressure hoses), rubber systems reinforced by fibres are used. The rubber matrix allows flexibility in bending, whereas the fabric reinforcement limits the in-plane stretching of the product. Raw rubber is known to have plastic-like deformation which behaves like an elastomer (i.e., a material that can undergo large elastic deformations which are reversible) only after crosslinking by vulcanisation.

There are also specialty rubbers which have certain properties. For example, butyl rubbers have low air permeability, nitrile rubbers have good oil resistance, and silicone rubbers have low temperature resistance.

As thermosets, rubbers are composed of molecules in 3D networks. In contrast with classical thermoset systems, for rubbers, it is more common to prepare high molecular weight polymer molecules first, and then crosslink them (only polyurethane (PU) rubbers are an exception to this rule). To facilitate (chemical) crosslinking for rubbers (which is also called vulcanisation), polymer chains with unsaturated carbon bonds are needed. If all the chains are saturated, appropriate copolymerisation with 1–2% of a monomer can introduce unsaturated groups. The original crosslinking (vulcanisation) agent for NR is a mixture of (2–3%) sulfur plus an accelerator. On heating to 140 °C, the sulfur reacts with C=C bonds on neighbouring chains to form sulfur crosslinks C-(S)-C. Typically, 15% of the crosslinks introduced are monosulfide (n = 1), about 1.5% are disulfide, and the rest are polysulfide (with n>2). The polysulfide crosslinks are partially labile (they can break and reform with other broken crosslinks if the applied stresses are high, leading to permanent creep in the compressed rubber blocks),
which can be avoided by producing only monosulfide crosslinks through the use of ‘efficient’ vulcanisation systems.

Rubber networks are characterised by average network chain molecular weights (between the crosslinks): $M_c$. A $M_c$ gram of rubber contains 1 mole of network chains (containing Avogadro’s number (NA) of network chains). Because 1 m$^3$ of rubber has a mass of 1000 dg (where $d$ is the density in kg/m$^3$) and contains $N$ network chains (where $N$ is the density of network chains), the density of the network chain will be related to the molecular weight of the network chain by:

$$M_c/1000 \ d = \frac{NA}{N} \ (1.1)$$

If the crosslinks are all connected to four network chains, then every additional crosslink increases the number of network chains by two, and so the density of crosslinks is $N/2$. Hence, the molecular weight of the network chain is inversely proportional to the density of crosslinks [3].

Table 1.1 summarises some of the characteristics of several polymers.

### 1.2 Polymeric Materials Commonly Used for Textiles Coating

In addition to several types of thermoplastics (e.g., PVC/polyvinylidene chloride (PVDC), polyvinyl acetate (PVA), polyurethanes (PU), acrylics), almost all types of (natural and synthetic) rubbers are commonly used for the coating of polymer textiles.

Thermoplastics used in textile coating will be the main subject of this chapter; rubbers will be presented in the next chapter.

Most of the properties of thermoplastics are useful for coating because they can be used as hot-melt adhesives and can be welded by heat. The polymer to be selected is expected to have certain properties, in addition to appropriate molecular weights to provide the requisite mechanical properties with appropriate values of $T_m$ and $T_g$. 
### Table 1.1 General Characteristics of Some Polymers

<table>
<thead>
<tr>
<th>Type of Polymer</th>
<th>Abbreviation Used</th>
<th>Tg(ºC)</th>
<th>Tm(ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermoplastics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) <strong>Commodity (Thermo) Plastics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene Low Density</td>
<td>(LDPE)</td>
<td>-120</td>
<td>115</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>(PP-iso)</td>
<td>-20</td>
<td>165</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>(PVC)</td>
<td>85</td>
<td>(220)*</td>
</tr>
<tr>
<td>Polyvinylidenechloride</td>
<td>(PVDC)</td>
<td>-17</td>
<td>(185-200)**</td>
</tr>
<tr>
<td>Polylacticate</td>
<td>(PVA)</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(PS)</td>
<td>100</td>
<td>(amorphous/atactic)</td>
</tr>
<tr>
<td>(ii) <strong>Engineering (Thermo) Plastics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene High Density</td>
<td>(HDPE)</td>
<td>-135</td>
<td>130</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>(PET)</td>
<td>69</td>
<td>265</td>
</tr>
<tr>
<td>Polyamide</td>
<td>(PA) (PA6)</td>
<td>50</td>
<td>215</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>(PC)</td>
<td>145</td>
<td>(295)*</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>(PMMA)</td>
<td>105</td>
<td>(amorphous)</td>
</tr>
<tr>
<td>Polycrylonitride</td>
<td>(PAN)</td>
<td>90</td>
<td>(*)</td>
</tr>
<tr>
<td>Liquid crystal polymer</td>
<td>(LCP)</td>
<td>-</td>
<td>420</td>
</tr>
<tr>
<td>(iii) <strong>Speciality (Thermo) Plastics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>(PTFE, or Teflon)</td>
<td>20</td>
<td>(327)*</td>
</tr>
<tr>
<td>Polyetheretherketone</td>
<td>(PEEK)</td>
<td>145</td>
<td>335</td>
</tr>
<tr>
<td>Thermoplastic Polyurethane</td>
<td>(PU)</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td><strong>Rubbers</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(i) <strong>Commodity rubbers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural rubber (Polyisoprene)</td>
<td>(NR)</td>
<td>-73</td>
<td>-</td>
</tr>
<tr>
<td>(Polybutadiene)</td>
<td>(PBD)</td>
<td>&lt; -90</td>
<td>-</td>
</tr>
<tr>
<td>Styrene-butadiene rubber</td>
<td>(SBR)</td>
<td>-copolymers 25/75-</td>
<td>-55</td>
</tr>
<tr>
<td>Polyurethane rubber</td>
<td>(PUR)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii) <strong>Speciality rubbers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl rubbers (Polyisobutylene)</td>
<td>(BR)</td>
<td>-70</td>
<td>0</td>
</tr>
<tr>
<td>Silicone rubbers (Polydimethylsiloxane)</td>
<td></td>
<td>-125</td>
<td>-55</td>
</tr>
<tr>
<td><strong>Thermosets</strong></td>
<td></td>
<td></td>
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<tr>
<td>Epoxy resins</td>
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<tr>
<td>Phenolic resins (Phenolics)</td>
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<tr>
<td>Polyester resins</td>
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<tr>
<td>(*) decomposes</td>
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<td>(**) softening point</td>
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</table>
The most commonly used thermoplastic polymers applied for textiles coatings are as follows:

- PVC
- PVDC
- PVA and acetate copolymers
- Acrylcs
- PU
- Others

In addition, for several special applications, other thermoplastics (e.g., polyimide and PTFE) can also be used. In more sophisticated applications (e.g., those leading to inherently electrically conducting textile-coated systems), other selected polymers (e.g., polypyrrole) can also be employed.

1.2.1 Polyvinyl Chloride

Polyvinyl chloride is a product of polymerisation of its monomer ‘vinyl chloride’. The latter is gaseous with strong carcinogenic properties. It has an International Agency for Research on Cancer (IARC) rating of A1, which means that it is a confirmed carcinogen in humans. (All chemicals used in the textile industry are subject to Control of Substances Hazardous to Health (COSHH) regulations, March 1994/1999, and to EC Directive 91/155/EEC). All chemicals used in the textile industry are subject to the ‘COSHH regulations’ (Control of Substances Hazardous to Health), March 1994/1999 and to EC Directive 91/155/EEC.

PVC and PVDC are also known as ‘vinyls’ or ‘vinyl resins’. PVC is one of the most widely used commodity polymers. It is a white, water-insoluble thermoplastic resin mainly used for coatings, insulation and piping. PVC has been used to make ‘linoleum’ for floors. In the 1970s, it was often used as vinyl tops for automobiles. It has a density of 1.38 g/cm$^3$ at 25 °C.

PVC was created accidentally by the German chemists Baumann (1872), and Katte (1912). Its potential was discovered later by the American chemist Semon (Goodrich, 1926). Patents for PVC were first taken out by Katte (until 1925), and Semon (after 1926). According to the Vinyl Institute in the USA, PVC is ‘unusual’ because it is partially (weight percentage-wise, at least) based on hydrocarbons (i.e., ethylene...
obtained from natural gas or petroleum), whereas most of it is based on the salt (for chlorine). It has repeating units of \( \text{C}_2\text{H}_3\text{Cl} \) along the polymer chain.

The suspension polymerisation technique is primarily used for the production of PVC. About 20% of PVC is made by solution, bulk, and emulsion polymerisation. The products obtained from suspension polymerisation and mass polymerisations are porous and hence can absorb plasticisers easily. The products of emulsion polymerisation are non-porous fine particles. Emulsion types, only if heated to >80 °C, can absorb plasticisers rapidly. Emulsion-type PVC is particularly important for the preparation of coats via organo-plastisols or plastisols.

PVC (Figure 1.1) is a thermoplastic. It softens/fuses into a highly viscous rubbery phase if heated above the \( T_g \) and hardens if cooled below the \( T_g \); this cycle can be repeated many times. \( T_g \) is known as a characteristic of amorphous region properties, and it is a particularly important decisive factor for PVC for determining its thermal and mechanical properties. PVC has typical dimensional stability up to its \( T_g \) with good creep resistance, low shrinkage, good impact resistance (except notch sensitivity), and good transparency. The \( T_g \) of PVC is ~80 °C [4].

![Structural formula of PVC](image)

Figure 1.1 Structural formula of PVC

PVC primarily has an amorphous structure (with crystallinity of ~10%). Being amorphous, PVC has no distinct melting point and undergoes a significant change in properties within the temperature range 170–180 °C with decomposition at higher temperatures (220 °C), with the splitting off of HCl. PVC is relatively unstable to heat and ultraviolet (UV) light, and certain stabilisers (for example salts of barium, cadmium, epoxy plasticisers, lead, or tin) are commonly used to improve its stability. Both thermal and light degradations proceed via chain reactions after being initiated by loss of a chlorine atom from the chain, and in the presence of oxygen. Both degradation reactions are accelerated in the presence of oxygen.
PVC can not be processed alone due to its rather low thermal stability and high melt viscosity; and combination with suitable additives is necessary during it’s pre-processing. The proper appropriate mixture with PVC and the additives (called as ‘the compound’) is then converted to a gelled material by heat and shearing, and is than processed. The additives used provide easy processability, as well as, giving a wide range of desired properties for different end-use applications after the processing. In fact, through appropriate formulation, a huge number of different PVC-systems can be planned and generated, which makes PVC as one of the most commonly used commodity plastics. One of these applications is in textile coating.

PVC compounds are, in generally formulated by using plasticisers (a wide variety of low or medium molecular weight chemicals, also termed as ‘flexibilisers’), to yield to materials with properties ranging from rigid to soft and flexible, can be produced simply by varying the plasticiser contents, from a few percent to more than >60% percent, respectively. Plasticised PVC, is the preferred form to use in textile coating, whereas rigid PVC can be obtained from blend compounds without plasticisers, and are known as ‘unplasticised PVC’, or ‘rigid vinyl’. Since pure PVC is hard and brittle, it must be softened properly by the use of plasticisers, for application as a coat.

Plasticisers function by lowering the $T_g$ (if flexibility at ambient temperature is needed, lowering the $T_g$ to below room temperature is necessitated). This can be achieved by the use of effective plasticisers (compatible chemicals with permanent features, also called ‘external plasticisers’) or by using appropriate copolymers to alter the main molecular structure of the main polymer chain (e.g., vinyl chloride-vinyl acetate copolymer, also called ‘internal plasticisation’).

External plasticisers are liquids of negligibly low volatility that are compatible with the polymer. Plasticisers are classified according to the degree of compatibility with the polymer matrix. Primary plasticisers are highly compatible with the polymer matrix and have permanent properties. Secondary plasticisers have limited compatibilities and are usually employed to introduce special properties to the system other than mechanical properties or to reduce cost.

Within primary plasticisers for PVC, there are:

- Phthalates (mainly C$_8$, including di-2-ethylhexyl phthalate and diisoctyl phthalate).
- Phosphates (mainly organic esters of phosphoric acids), the most important characteristic being $T_g$ (i.e., tricresyl and trixyll, which also provides fire retardance).
- Epoxides (epoxidised soybean or linseed oil).
Polymeric plasticisers (mostly saturated polyesters).

Secondary plasticisers include aliphatic diesters (esters of adipic, azelaic and sebacic of certain branched alcohols), which also provide low temperature flexibilities to PVC.

The liquid compositions of PVC with plasticisers are usually produced from lattices obtained from the emulsion polymerisation of vinyl chloride. These are then dispersed into plasticisers to make plastisols, or into mixtures of plasticisers and selected other organic liquids to make organosols. Plastisols are also termed ‘pastes’.

In such compounds, in addition to plasticisers, there are several other additives are used. These include UV/radiation and heat stabilisers, antioxidants, fire retardant chemicals, pigments, coupling/bonding agents, colorants, blowing agents, and even fillers [5, 6]. PVC particles remain dispersed in the liquid until the mixture is subsequently heated to >120 °C; the mass gels and fusion occurs, yielding the solid coat with, in the case of organosols, loss of solvent.

There are several typical textile products with PVC coatings. These include: tarpaulin (which is the main outlet for PVC plastisol-coated polyester or Nylon woven fabric [7]); awnings (usually with PVC, PP or acrylic polymeric coats on Nylon, polyester or textile); tents of different sizes (in general, smaller ones are made of PU and the larger ones of PVC or Neoprene-coated polyester/Nylon woven fabrics); upholstery items (mainly transfer-coated PVC with expanded grades for a soft touch) and in protective clothing (e.g., PU transfer-coated items); ‘leather cloth’ materials for garments and luggage (from PVC transfer coating); and banners and bunting.

Some of the main advantages and disadvantages of using PVC as a coating are summarised next.

The advantages of using PVC as a coat are:

- PVC is a versatile, economical polymer.
- PVC has good resistance against oil, solvent and abrasion; it also has advantages with respect to heat and radio frequency weldability.
- PVC can be readily compounded with a series of different additives (including plasticisers).
- PVC has inherent good fire retardant resistance (which can be further improved).

The disadvantages of using PVC as a coat are:

- PVC tends to crack when cold.
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- If PVC is prepared with plasticisers, there is the danger of plasticiser migration. This has drawn strong criticism from environmentalists when classical plasticisers (e.g., phthalates) have been employed [8], mainly because of their possible biochemical effects. Now, in almost all countries, the use of new, safer alternative plasticisers (‘green plasticisers’) has been enforced. In addition to plasticisers, other possible contaminants (e.g., various stabilisers and heavy metal ions) should be considered.
- PVC has moderately low heat resistance.
- PVC has low ageing resistances.

PVC-coated textiles have several architectural applications [7]. It is the most common polymeric coating material used in the production of tarpaulins and tents. Its use in upholstery (‘synthetic leather’) and as protective clothing are also very common.

1.2.2 Polyvinylidene Chloride

Along with PVC, PVDC is a member of the ‘chloropolymers’ family. It is a thermoplastic vinyl polymer.

PVDC is the polymerisation product of vinylidene chloride monomer (VDC) in emulsion. Its emulsions are used to impregnate mainly fabrics, leather and paper. PVDC polymer is physiologically harmless, and has repeating units of \( \text{C}_2\text{H}_2\text{Cl}_2 \) along the polymer chain (\(-[\text{CH}_2-\text{CCl}_2]-\)). It is a strong polymer with high tensile and flexural strengths. It is a white powder with a softening temperature range of 185-200 °C. PVDC is used to products with properties ranging from soft-flexible to rigid. The degree of crystallinity can be \( \leq 50\% \), and density (at 30 °C) is ~1.87 g/cm\(^3\). PVDC is combustible but self-extinguishing, and may release HCl gas when heated.

PVDC is invented incidentally by a laboratory worker and a college student (Wiley, Dow Chemical, 1933). Its first application was by the military. They sprayed PVDC on fighter planes to guard against salty sea spray. In addition, car-makers used it for upholstery. The most popular use came in 1953, when Saran Wrap was introduced. In 2004, however, the formula was changed to LDPE out of environmental concerns about the chloride existing present in PVDC.

PVDC (Figure 1.2) is largely used as a clear, flexible and impermeable food wrap. PVDC Shrink (also called ‘cling film’ or ‘cling wrap’), is a thin, plastic film (Saran Wrap).
The advantages of using PVDC as a coat are:

- PVDC has exceptional fire retardancy properties which can be further improved by blending it with PVC.
- PVDC has very low permeability to gases, so it is considered to be almost perfectly impermeable to gases (i.e., vapours, moisture and oxygen).
- PVDC is clear/transparent with high gloss.
- PVDC is heat-weldable.
- PVDC can be readily blended with PVC and acrylics and, because of this property, it is usually used to improve the fire retardancy of coatings.
- There is practically no effect of sunlight on PVDC.
- PVDC is resistant to strong acids and bases (except 95% sulfuric acid, as well as concentrated solutions of NaOH and NH₃).
- PVDC is sensitive to electron irradiation and light.
- The thermal properties of PVDC are similar to that of PVC, therefore there are certain difficulties involved in its processing and stabilisation.

The disadvantages of using PVDC as a coat are:

- PVDC is more brittle than PVC and can easily crack if cold.
- PVDC is soluble in most organic solvents.
- The monomer, VDC, is an irritant and is genotoxic.
- Although it burns with difficulty, it burns with a green flame, producing a pungent odour and evolves the toxic gas HCl.
- PVDC can turn yellow or brown if exposed to alkalis.
1.2.3 Polyvinyl Acetate and Acetate Copolymers (Ethylene Vinyl Acetate)

Polyvinyl acetate (PVAc) is the polymer of vinyl acetate; polymerisation is usually in suspension or emulsion. It is a vinyl ester, and is completely amorphous. PVAc (Figure 1.3) is used primarily in the form of emulsions, and it is also the precursor of polyvinyl alcohol and poly(vinyl acetal).

\[
\begin{align*}
\text{CH}_2 \text{CH} & \quad \text{O} \\
\text{O} \quad \text{CH}_3 & \quad \text{O}
\end{align*}
\]

*Figure 1.3 Structural formula of PVAc*

The representative polymer in this group that is widely used in textile coating is EVA polymer (polyethylene vinyl acetate copolymer). It is commonly used as a backing material for carpets and upholstery as well as the coat for wall coverings (although the polymer itself is used widely as an adhesive).

The advantages of using PVAc as a coat are:

- PVAc gives good adhesion to almost all types of polymers with very good binding properties
- PVAc is flexible at low temperatures
- PVAc is economically feasible
- PVAc is readily heat-weldable
- PVA is stable to light

The disadvantages of using PVAc as a coat are:

- The polymer is sensitive to water: it has poor wash resistance and dissolves readily in common solvents
- Over time, the polymer may show some discoloration
The copolymerisates of PVAc include ethylene-vinyl acetate, but they can be acrylic esters, vinyl esters or vinyl chloride. Each has different properties (e.g., the copolymerisate with vinyl chloride yields water-resistant polymers with higher hardness characteristics).

1.2.4 Acrylics (Acrylic Polymers)

Acrylic polymers are very common, and have a range of properties and prices. They are mainly used as back coatings for upholstery (fabric and carpets), as adhesives for laminates, and as lacquers for tarpaulin. The polymer itself is used as an adhesive.

The general formula for acrylics (as represented by acrylic ester) is shown in Figure 1.4.

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{n} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{R'} \\
\end{array}
\]

**Figure 1.4 Structural formula of acrylic esters**

In this group of polymers, there are mainly acrylates (where R is replaced by H in the formula shown above) and methacrylate polymers (R is replaced by \( \text{CH}_3 \)). In methacrylates, the most important member is PMMA, in which \( \text{R} \) and \( \text{R} \) are \( \text{CH}_3 \). The characteristics of different \( \text{R} \) and \( \text{R}' \) groups give rise to different acrylates with different properties. PMMA is made from the monomer methyl methacrylate (MMA). In general, acrylates are soft and tacky, whereas methacrylate polymers are hard and brittle.

Acrylic polymers are prepared by bulk, suspension, solution, or emulsion polymerisation. The products of the latter solution and emulsion polymerisation are preferably used for coatings. Acrylic resin coats, as waterproof coatings, are successfully applied on woven Nylon or polyester substrates with ‘crushed foam coating’ for curtains [9]. Modern car seats are usually back-coated with acrylics to increase abrasion resistance and to improve fire resistance.
The advantages of using acrylic polymers as a coat are:

- Acrylic polymers have good clarity.
- They have high UV resistance.
- Acrylic polymers are with good resistances.
- Acrylic polymers have good resistance to ozone aging.
- They have exceptional resistance to various chemicals and water.
- Acrylic polymers can be considerably very economical.
- They can be blended with a range of other polymer types (mainly with PVC and PVDC).

The disadvantages of using acrylics as a coat are:

- The fire retardance resistance of acrylics is very poor, and acrylics have to be used by compounding with fire retardant agents.
- The monomer, MMA is toxic and, according to the IARC, is not carcinogenic [6]. MMA can exist in the bulk of the polymer as a remnant, or can also be produced from the thermal degradation of PMMA.

1.2.5 Polyurethane

PU (Figure 1.5) are a family of polymers produced by the polyaddition reactions of di-or polyisocyanate with a di- or polyfunctional alcohol (polyol) [2]. They contain the (-NCOO-) group.

\[
\text{OCN} \begin{array}{c} \text{[-]} \end{array} \begin{array}{c} \text{R - NH - C - O - R'} \end{array} \begin{array}{c} \vdots \text{(-)} \end{array} \begin{array}{c} \text{O - C - NH - R} \end{array} \begin{array}{c} \vdots \text{(-)} \end{array} \begin{array}{c} \text{R - NH - C - O - R'} - \text{OH} \end{array}
\]

<table>
<thead>
<tr>
<th>O</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>R'</td>
</tr>
</tbody>
</table>

\[n - 1\]

\[O\]

\[O\]

**Figure 1.5 Structural formula of urethane**

In the general formula of the urethane molecule presented above, variations in the R and R’ groups provide several possibilities for different types of urethanes to be
produced. Various chain extenders (such as short-chain diols or diamines) are usually employed in the synthesis of PU polymers.

Isocyanates: within the different types of isocyanates employed, there are aliphatic isocyanates (e.g., toluene diisocyanate, and hexamethylene diisocyanate as well as aromatic isocyanates (such as diphenyl methane diisocyanate, in addition to naphthalene 1,5-diisocyanate, xylene diisocyanate, \( p \)-phenylene diisocyanate and 3,3’-tolidine diisocyanate).

If aromatic isocyanates are used in the production of PU, the product usually rapidly becomes yellow upon exposure to the light. Hence, several aliphatic and cycloaliphatic diisocyanates (e.g., isoprene diisocyanate, cyclohexyl diisocyanate and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate) are used for the production of PU. The PU become much more light-resistant and are extensively used for coatings.

Polyols (polyfunctional alcohols) are the second important component in the structure of PU.

There are mainly two types of polyols used: polyester (or polyether) polyols, with at least two hydroxyl groups in a polyester (or in a polyether chain), are used. Polyester polyols are saturated dicarboxylic esters (see Figures 1.6 and 1.7).

\[
\begin{align*}
H - [ \text{OR} - \text{OOCR'} - \text{CO} \ldots - ]_n \text{OROH}
\end{align*}
\]

**Figure 1.6** Polyester polyl

\[
\begin{align*}
\text{HO} - \text{R} - \text{O} - [\text{C} - (\text{CH}) - \text{O} - ]_{2,5} \text{H}
\end{align*}
\]

**Figure 1.7** Caprolactone polyester
Polyether polyols are polyalkylene glycols (or polyalkylene oxides) (see Figures 1.8 and 1.9).

\[ H - [ - O - CH - CH - ...] - OH \]

*Figure 1.8 Polypropylene glycol*

\[ H - [ - O - ( - CH - ) - ] - OH \]

\[ \text{H} \quad 2 \quad 4 \quad n \]

*Figure 1.9 Polytetramethylene glycol*

PU are prepared mainly by one of two methods: the ‘one-shot’ or ‘prepolymer’ process.

(i) In the one-shot method, the polyol, diisocyanate, chain extender and catalyst(s) are mixed together simultaneously and PU is produced with an exothermic reaction (Figure 1.10).

\[ \text{OH} \quad \text{OH} + \text{OCN-R'-NCO} \rightarrow \text{PU polymer} \]

*Figure 1.10 The one-shot process in PU production*

(ii) The prepolymer process occurs in two steps. In the first step, diisocyanate and polyol are used to produce an intermediate polymer (a prepolymer) of low molecular weight. This is then reacted with a chain extender (polyfunctional alcohol or amine) to form the final PU product with sufficiently high molecular weight in the second step (Figure 1.11).
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\[
\text{OH} \quad \quad \text{OH} + \text{OCN-R'}\text{-NCO} \quad \Rightarrow \quad \text{OCN} \quad \quad \text{NCO} \\
(\text{or OH} \quad \quad \text{OH})
\]

Prepolymer

Polyol diisocyanate

This first step is succeeded by the following second step:

prepolymer -- chain extension by diol/diamine PU polymer

\textbf{Figure 1.11} Prepolymer (two-step) process in PU production

Most PU prepared have a segmented (block copolymer) structure composed of alternating ‘soft segments’ of polyol and ‘hard segments’ produced by the reaction of diol/diamine/diisocyanate. This gives rise to a heterodisperse two-phase structure of dispersed discrete hard-segment domains in a matrix of soft segments. Aggregated dispersed hard segments help to tie the polymeric chains acting as physical (virtual) crosslinks and reinforce the chains in the soft matrix. These linear PU systems are elastomeric because of this structure; the physical crosslinks due to the hard-segment domains help to provide elasticity, in addition to the soft matrix with \(T_g\) values lower than ambient temperature. They also have thermoplastic properties, being reversible to heat and solvation, both of which are important for thermoforming and solution applications. These linear PU with physical crosslinks are also called as ‘thermoplastic urethanes’ (TPU).

In TPU systems, the matrix is usually amorphous, whereas hard segments are paracrystalline or crystalline. PU systems with chemically introduced crosslinks (with chemical crosslinks, thermoset PU) may have similar morphological structures.

PU coatings of polyurethane have very good resistance to abrasion and solvent attack, and have good flexibilities and impact resistances. PU coatings are mainly prepared by conventional solution-based techniques, which use one- or two-component systems. They can be applied by dip, spray or brush techniques and adhere very well to various materials. In addition, there is the ‘hot melt’ process, which is solvent-free [10].

The one-component system can be a reactive one component system (using low molecular weight prepolymers with terminal isocyanate groups dissolved in low polar solvents applied as a coat directly, with water at ambient temperature acting as a chain extender and crosslinking agent) or a completely reacted one component
Thermoplastic Polymers Used in Textile Coatings

system (where high molecular weight PU is dissolved in a highly polar liquid (e.g., dimethyl formamide) and dried by physical means).

For two-component systems, a solution of the polyisocyanate component (with isocyanate-terminated prepolymers or polyfunctional isocyanates) is mixed with a polyhydroxy component to prepare the material, which is then applied as the coat.

For ‘green coating’ purposes, aqueous dispersions PU are also employed, in which lattices composed of PU-urea elastomers are dispersed in water with the aid of appropriate emulsifiers.

PU coatings are specifically preferred if unusual impact and abrasion resistances are required (e.g., floors in public buildings), as well as for various outdoor and marine uses (due to their good weatherability). PU coatings are used to produce tents of different sizes (in general, smaller ones of PU and the larger ones of PVC or Neoprene coated polyester/Nylon woven fabrics), in upholstery (mainly transfer coated PU with expanded grades for a soft touch) and in waterproof protective clothing (i.e., mainly with PU transfer coated items). Other examples include luggage, footwear, glove and waterproof mattress covers, as well as imitation leather and suede from coagulated PU [11, 12].

In brief, the advantages and disadvantages of using PU coatings on textiles or on any substrates are listed next.

The advantages of using PU as a coat are:

- PU coatings are extremely tough with very high tensile/tear/impact resistance and very good abrasion resistance.
- Their weatherabilities are very good.
- They are flexible at low temperatures with leather-like properties.
- The property of the coat can be prepared on demand. That is, the property is dependent upon the type of polyol, the molecular weight, and the ratio of hard to soft segments used in their production.
- PU coatings can give a wide range of improved properties to the substrate, including breathable microporous characteristics.
- PU coatings can be dry-cleaned (plasticisers are not used). For TPU, no curing is needed.
- PU coatings, in general, provide good adhesion to fabric substrates, have good elongation and excellent flexibilities.
The disadvantages of using PU as a coat are:

- Polyols are considered to be relatively non-toxic. However, isocyanates are highly toxic. Hence, the PU product can show significant toxicity if any remnant of isocyanate is left within it (down to 0.02 parts per million (ppm)). If such products make contact with the skin, they may produce redness leading to blistering, even to a series of possible respiratory complications upon prolonged contact [6].

- In the case of fire, even flame-retarded grades of PU can generate toxic fumes of carbon monoxide and cyanic acid

1.2.5.1 Polyurethane Foams

In the production of PU foams, excess isocyanate groups in the polymer chain react with water (or carboxylic acids) to produce carbon dioxide. The latter blows the foam as well as simultaneously affecting the crosslinking. PU foams can be in flexible or rigid forms, mainly depending on the nature of the polymer and the type of crosslinking produced. Their production is also a multi-step process: if a bifunctional intermediate is produced, there will be flexible foams; if a polyfunctional intermediate is used then rigid foams result.

In flexible foams, the intermediate is usually reacted with an aromatic diisocyanate (e.g., tolylene diisocyanate), and tertiary amine (or stannous soap) catalysts are used, leading to crosslinks with urea linkages. This process is also suitable for one-shot processing.

1.2.5.2 Polytetrafluoroethylene Coatings

PTFE coatings are already existing since years in a number of have been used in architectural applications (e.g., the Millenium Dome, London, UK is constructed from PTFE-coated glass fibre fabric with an estimated life time of 25 years as a ‘permanent structure’, [9]) and various other coated textile structures [13, 14]. Although the cost implications of using the economy with PTFE coatings do not initially seem favourable, when the performance and life times of coated textiles are considered, it they usually becomes a the preferred solution, giving rise to ‘more permanent structures’. Due to the high price, its common applications are rather restricted, and are mainly used for gaskets, seals and calender belts.

PTFE is inherently fire-resistant, which is an added advantage. PTFE is inert to most chemicals and have has excellent high resistance to UV radiation, oxidation and weathering. With its unique ‘non-stick’ properties, it gives rise to ‘mould-
stain-free, long-term clean’ surfaces. PTFE provides a quite wide service temperature (≤ up to 260 °C).

1.2.5.3 Polyolefin Coatings

In this group of polymers, there are PE (LDPE and HDPE), and PP is used for textile coating. Polyolefin coatings are mainly used for tarpaulins as an alternative to PVC, for lightweight coverings, and for bulk bags and sacks of various sizes.

All three of the polymers (HDPE, LDPE and PP) have good resistance to acids, alkalis and chemicals. Their densities are small (i.e., they have a light weight for the same thickness of coat). They are low cost to use. However, their low melting points and virtually absent fire-resistance properties, in addition to limited resistances to weathering, are the main disadvantages.

References


