“Innovative process eco-sustainable with new polymer coatings for steel wires”

Preparatory action A.1

Report on Plastic Materials for Extrusion

Authors: Maurizio Fiorini, Laura Sisti and Martino Colonna

Centro Interdipartimentale di Ricerca Industriale
Edilizia e Costruzioni
Alma Mater Studiorum Università di Bologna
Via Terracini 28, 40131 Bologna, Italy
FOREWORDS

This report has been prepared to fulfill a request made by Officine Maccaferri. CIRI Edilizia e Costruzioni was awarded writing this report with the aim at supporting the activities of LIFE.Inno.Pro:Wire project.

Part A focuses on polymer materials, providing data on World consumptions, trends and some forecast on future developments. Then, the main families of thermoplastic materials are reviewed with respect to production processes and, properties.

Part B deals with extrusion process technologies, focusing on screw design as it has a strong influence on extrusion performance. At the end of the second part, a section on polymer adhesion on metal underlines the importance of interface for attaining the desired product performances.
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1. World plastics production data

Data presented here were collected from reports by Plastics Europe (the Association of Plastics Manufacturers in Europe), EuPC (the European Plastics Converters), Plastics Recyclers Europe and EPRO (the European Association of Plastics Recycling and Recovery Organizations).

Global plastics production rose to 288 million tonnes in 2012, with an 2.8 % increase compared to 2011 (Figure 1). The exponential growth observed over the last 60 years is a reflection of the expansion of downstream demand and the incorporation of plastic products into every facet of modern life. From a production of about 2 million tonnes in 1950, the production reached 288 million tonnes in 2012, a 169 fold increase.

The global downturn after 2008 crisis exposed the cyclicality of plastic demand with production actually declining, though volume has since recovered. In Europe, in line with the general economic situation, plastics production decreased by 3% from 2011 to 2012.

![Figure 1. World and European plastics production 1950-2012. (Data includes other plastics: thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants and PP fibers. Not included PET-, PA- and polyacryl-fibers).](image)

The plastics growth is far from over. From one side, innovation will play its part in stimulating further demand. From the other side, urbanization and increasing wealth in the developing countries will support growth rates (Figure 2).

Global per capita consumption growth has been forecast at 4% per annum in 2011. The downturn in Europe and in part in North America may affect slightly this forecast, as Asia closes the gap with more developed markets (24 kg/year per capita versus 120 kg/year). Every 1 kg increase in per capita consumption in Asia (excluding Japan) equates to an approximate increase in demand of 4 million tonnes. This is 1.4% of the 2012 global production and about 10% of China’s 2012 consumption. These trends are supported by different studies published by Plastics Europe (Figure 3) and BASF (Figure 4).

![Figure 2. Plastic demand by converters per capita per region](image-url)
China confirms its role as world leading plastics producer, with a 23.9% share of the global production. Combining China’s with the rest of Asia and Japan Figures, Asia turns out to be the top producer of plastics, with a share of 44.6%. Asia is also the largest market, even if the per capita consumption is much lower than developed markets. In Europe, Germany is by far the largest market, accounting for about one fourth of total European demand. Italy follows far behind, totaling about 14.3% of the European demand. These two major consumers, along with France, UK, Spain and the Benelux countries makes up almost 75% of the total demand in the EU. Western European showed a decline in demand (-3%), whereas Central European countries showed an increase (+0.6%) (Figure 5).
World plastics demand is divided in many industry sectors. Top three sectors in particular account for greater than 67% of this demand. Namely, they are plastic packaging, building and construction and motor vehicle (mainly automotive), see Figure 6. Population growth, rising disposable incomes,
urbanization and changing lifestyle are anticipated to drive the developing markets demand for many years to come (Figure 7).
In Europe, the plastics demand by segment is reflecting the global trend with some small differences (Figure 8). Among the sectors combined altogether as “Others”, healthcare products show the highest growth rate.

![Figure 8. European plastics demand by sector (EU-27 plus N and CH).](image)

**Packaging**

The use of plastics in packaging has increased rapidly over the past 30 years with packaging now the single largest downstream consumer of plastics and that growth will continue. According to a study by Smithers Pira Research, an increase in value of over 20% in the 6 years 2010-2016 is forecast.

Robust growth in demand for rigid plastic packaging especially in sectors like drinks, cosmetics, toiletries, household and personal care products, is stimulating packaging consumption.

Flexible plastic packaging materials are receiving a boost from perishable foods, healthcare, convenience food and various industrial markets.
Food and healthcare packaging are the biggest end user markets of global packaging. The estimated USD 43 billion increase in the food industry by 2016, along with 4.5% and 4.2% year on year increase in health care and cosmetic packaging are going to fuelling future growth. These combined trends lead to a 22% forecast increase in the value of the packaging industry between 2010 and 2016.

Packaging consumption is highly correlated with GDP and disposable income. Unsurprisingly the US was the largest consumer of packaging in 2012, 70% larger than second placed China. Increasing disposable income in developing regions is fuelling consumptions across a broad range of products. High Asian growth rates are changing consumption patterns. China is anticipated to surpass US consumption by 2017, while demand in India is set to nearly double over the years 2010-2015, raising it among the top 10.

**Building and construction**

Demand for pipes, switches, insulation and flooring materials by the construction industry makes this the second largest consumer of plastic products, both in the world and European markets. The highly cyclical nature of construction creates volatility in plastic demand as witnessed during 2008 and early during 2009. Restored consumer confidence and economic recovery is expected to increase demand for plastic building materials. Global Industry Analyst Inc. estimated the demand for plastic pipes to reach 7.6 billion meters by 2017, largely driven by increased infrastructure investment and construction activity in developing countries.

**Automotive industry**

Global automotive plastics had an estimated turnover of USD 22.2 bn in 2011 and it is forecast to grow at a compound annual growth rate (CAGR) 13.7% to 42.1 bn in 2016 as a result of increasing use of plastic products to improve aesthetics, noise reduction, and to reduce vehicle weight (which improves fuel efficiency and reduces carbon emissions).

Global automotive plastics consumption reached 7.1 million tons in 2012. The forecast 8.0% CAGR from 2013 to 2018 will end up to increase the market at 11.3 million tons in 2018. The high growth rate of the industry is attributable to increasing passenger car production and initiatives by automobile manufacturers towards light-weighting of cars.

As of 2012, Asia-Pacific leads consumption by capturing 50.5% of market followed by Europe (28%), North America (11.3%), and rest of the world (10.1%). Asia-Pacific is likely to remain the leading consumer of automotive plastics driven by passenger car production. In Asia the annual
growth is forecast at 8.8%, above the forecast global average of 7.2% through 2016. The increase in car production is underpinned by rising car ownership, increasing disposable income levels and falling auto loan rates.

The properties of plastics such as easy moldability, recyclability, scratch resistance, high volume to weight resistance, thermal stability, impact strength, and resistance to abrasion make them suitable for use in automobiles. Plastic materials can be found in any part of modern vehicles, in body parts and in the interior. Data reported in Figure 9 refer to the European car industry. Body parts include bumpers, fascia, lateral mirrors and fenders. Plastics play a major role in interior parts, (52.5%: upholstery, seating, dashboards). Even in demanding applications under the hood, where engine component temperature may go up to 200-220°C, plastics (specialty compounds based on glass filled PA and polyesters) play a role in components such as air intake manifolds, filters housing, oil sumps and crankshaft cover.

Figure 9. Plastics use in the automotive industry in Europe, 2012.
Although up to 13 different polymers may be used in a single car model (see Table 1), just three types of plastics make up some 66 % of the total plastics used in a car: polypropylene (32 %), polyurethane (17 %) and PVC (16 %).

Table 1. Average plastics consumption in cars

<table>
<thead>
<tr>
<th>Component</th>
<th>Main types of plastics</th>
<th>Weight in av. car (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bumpers</td>
<td>PS, ABS, PC/PBT</td>
<td>10.0</td>
</tr>
<tr>
<td>Seating</td>
<td>PUR, PP, PVC, ABS, PA</td>
<td>13.0</td>
</tr>
<tr>
<td>Dashboard</td>
<td>PP, ABS, SMA, PPE, PC</td>
<td>7.0</td>
</tr>
<tr>
<td>Fuel systems</td>
<td>HDPE, POM, PA, PP, PBT</td>
<td>6.0</td>
</tr>
<tr>
<td>Body (incl. panels)</td>
<td>PP, PPE, UP</td>
<td>6.0</td>
</tr>
<tr>
<td>Under-bonnet components</td>
<td>PA, PP, PBT</td>
<td>9.0</td>
</tr>
<tr>
<td>Interior trim</td>
<td>PP, ABS, PET, POM, PVC</td>
<td>20.0</td>
</tr>
<tr>
<td>Electrical components</td>
<td>PP, PE, PBT, PA, PVC</td>
<td>7.0</td>
</tr>
<tr>
<td>Exterior trim</td>
<td>ABS, PA, PBT, POM, ASA, PP</td>
<td>4.0</td>
</tr>
<tr>
<td>Lighting</td>
<td>PC, PBT, ABS, PMMA, UP</td>
<td>5.0</td>
</tr>
<tr>
<td>Upholstery</td>
<td>PVC, PUR, PP, PE</td>
<td>8.0</td>
</tr>
<tr>
<td>Liquid reservoirs</td>
<td>PP, PE, PA</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>105.0</strong></td>
</tr>
</tbody>
</table>

2. POLYOLEFINS
Polyethylene (PE) and polypropylene (PP) are the two main types of polyolefins. A schematic, somewhat simplified classification can be further expanded based upon: monomer/comonomer composition, catalyst/initiator system and polymerization reactor technology.

### 2.1 POLYETHYLENE

Polyethylene is the highest-volume polymer in the World, the demand reached about 85 million metric tons in 2013. This value accounts for little less than 40% of the world annual thermoplastic production. Polyethylene demand is estimated to grow up to 100 million metric tons in 2016. As a matter of fact, PE’s are classified by their density and there are three main families of polyethylene’s: low density (LDPE), linear low density (LLDPE) and high density (HDPE). In order of increasing volume, LDPE has a 9% market share, LLDPE a 11% and HDPE a 17%. In addition to these three main commercial grades, very low density polyethylene (VLDPE) is produced in much lower volumes and it finds applications where extremely high flexibility and optical clarity are required. Ultra high molecular weight polyethylene (UHMWPE) finds applications in medical sector, sport goods and mining industry (among others). PE offers a unique combination of useful properties at a very low price. The main advantages of PE are: high toughness, ductility, excellent chemical resistance, low water vapor permeability, very low water absorption, all combined with the ease with which it can be processed. The main limitations are the low melting temperature, low modulus and yield stress.

Ethylene polymerization on industrial scale is carried out exploiting one of the two different processes to promote chain growth: 1) high pressure, high temperature, radical initiated reactions; 2) insertion reactions on coordination catalysts. The two processes are schematically described below.

LDPE is made using free radical processes and contains short chain branches (SCB) along with long chain branches (LCB). Coordination catalysts can control polymer microstructure much more efficiently than free radical initiators.
Figure 11. (a): coordination step before ethylene insertion on a polyethylene chain (active site control); (b) Generic free radical polymerization (chain-end control)

By adding comonomers like \( \alpha \)-olefins (1-butene, 1-hexene and 1-octene are the cheapest and most widely used), SCB are inserted with a more precise control. LLDPE and HDPE are produced exclusively by coordination catalysis. The microstructure of different PE containing SBC along with LCB or SCB alone is described below.

Figure 12. Classification of polyethylene types according to branching structure and density
2.2 LDPE

High temperature, high pressure radical initiated ethylene polymerization was first developed in 1930’s. Since then, this technology has evolved and has been improved, leading to safer and more cost effective plants. From the point of view of polymerization chemistry, the main improvement has been the introduction of organic peroxide to initiate ethylene polymerization, instead of thermally activated initiation. In modern plants, ethylene is compressed by a hyper compressor (2000 – 3100 bar), then preheated to 150-170 °C and it is introduced into a tubular reactor. Reaction is initiated by injection of organic peroxides in the reactor, at multiple locations after each reaction peak, optimizing the temperature profile of the reaction mixture. In autoclave reactors, ethylene inlet flow from the compressor is split and injected to designed reactor points. An organic liquid peroxide is injected to maintain a continuous polymerization reaction at controlled temperature zones. EVA and acrylic-modified copolymer are also produced with this technology. For a modern, single-train tubular reactor, capacity up to 450 kt/y is attained. Autoclave reactor capacity is lower, 100 – 150 kt/y. The flowchart of the two different plants is reported below.

![Figure 13. Simplified process flow diagram of a LDPE plant using a tubular reactor (Courtesy Lyondell-Basell)](image)
High pressure ethylene polymerization is initiated by decomposition of an organic peroxide (or an azo compound) leading to the formation of a radical. A few examples are reported below.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroperoxide</td>
<td>( \text{ROOH} \rightarrow \text{RO}^\ast + \text{HO}^\ast )</td>
</tr>
<tr>
<td>Dialkyl peroxide</td>
<td>( \text{ROOR}^\ast \rightarrow \text{RO}^\ast + \text{RO}^\ast )</td>
</tr>
<tr>
<td>Tertiary perester</td>
<td>( \text{RCOOCR}^\ast_3 \rightarrow \text{RCO}^\ast + \text{R}^\ast_3\text{COCO}^\ast )</td>
</tr>
<tr>
<td>Azodialkyl</td>
<td>( \text{RNNR}^\ast \rightarrow \text{RN}^\ast + \text{R}'\text{N}^\ast )</td>
</tr>
</tbody>
</table>

R and R’ = an alkyl or aryl group or various other organic moieties.

Then, the radical reacts with ethylene relocating the unpaired electron at the opposite end of the monomer:

\[
\text{R}^\ast + \text{CH}_2=\text{CH}_2 \rightarrow \text{R}^\ast\text{CH}_2\text{CH}_2^\ast
\]

Polymerization then takes place by reaction of ethylene molecules from the gas phase with the radical on the end of a growing chain. High pressure is required in order to bring ethylene molecules in close contact to propagate the reaction chain.
Chain branching occurs when the terminal radical responsible for chain growth extracts an hydrogen atom from a preexisting polyethylene chain. The growth on the original chain is terminated and the propagation is started at the new radical location. SCB is the result of intramolecular radical transfer. LCB is the result of intermolecular radical transfer. Polymerization conditions control the frequency and type of chain branching, in general higher polymerization temperatures promote branching. The probability of intermolecular hydrogen abstraction, which leads to LCB, is proportional to the length of the molecule. Hence, LCB is more prevalent in high molecular weights.

SBC occurs when the growing chain end abstracts an hydrogen atom on itself, a few bonds away from the chain end. This reaction is called “backbiting”. The effect is such that chain growth starts on the new location along the chain (where hydrogen was abstracted), leaving the original growing chain as a short branch. Ethyl and butyl branching is prevalent.
The molecular weight of LDPE produced by radical polymerization is controlled by chain transfer reactions in which the growth of the chain on the original location is stopped and the free radical is transferred to another molecule. The chain growth resumes on this new location and as a result the number of radical and growing chains remains constant. Chain transfer takes place with ethylene or with other molecules (for example a solvent) deliberately added to control the molecular weight. Two examples of chain transfer are reported below.

\[
\begin{align*}
\text{CH}_2=\text{CH} \cdot + \text{CH}_2=\text{CH} & \rightarrow \text{CH} \cdot + \text{CH}_2=\text{CH} \\
\text{CH}_2=\text{CH} \cdot + \text{CH}_2=\text{CH} & \rightarrow \text{CH}_2=\text{CH} + \text{CH}_2=\text{CH} \\
\text{CH}_2=\text{CH} \cdot + \text{RH} & \rightarrow \text{CH}_2=\text{CH} + \text{R} \\
\end{align*}
\]

The complete termination of the chain growth takes place when two radicals react together and quench each other. At least one of them is a radical active in chain growth. One common termination reaction is radical coupling to form a new covalent bond. The following examples involve low molecular weight species:

\[
\begin{align*}
\text{CH}_2=\text{CH} \cdot + \text{CH}=\text{CH} & \rightarrow \text{CH}_2=\text{CH} \\
\text{CH}_2=\text{CH} \cdot + \text{RO} & \rightarrow \text{CH}_2=\text{CH}-\text{OR} \\
\end{align*}
\]

When two growing chain ends meet, the result may be chain coupling with formation of a single polymer molecule or disproportionation to leave the chain ends as separate molecules.

\[
\begin{align*}
\text{CH}_2=\text{CH} \cdot + \cdot \text{CH}_2 & \rightarrow \text{CH}_2=\text{CH} \\
\text{CH}_2=\text{CH} \cdot + \cdot \text{CH}_2 & \rightarrow \text{CH} + \cdot \text{CH}_2 \\
\end{align*}
\]

LDPE is hence characterized by a substantial concentration of SCB. These chain branching hinders the crystallization process, resulting in relatively low density. LDPE is produced with a density range 0.91 – 0.94 g cm\(^{-3}\). The degree of crystallinity is also lower than other PE grades, it may vary 42 -62 % (from density measurements) or 30 -54 % (from calorimetry). LCB are important to confer highly desirable properties to LDPE, including non-Newtonian rheological characteristics and high melt strengths combined with relatively low viscosities at the shear rate encountered during processing. These rheological properties make LDPE a material of election in film-blowing processes. Indeed, blown film is the principal outlet for LDPE, accounting for more than half of all
usage. Because of LDPE low crystallinity, films are transparent, soft to touch and moderately tough. The ready deformability and high creep of such films make them unsuitable for high load applications or situations in which prolonged low level stress is encountered. LDPE films are widely used in commercial and retail packaging applications. Other uses include diaper backing, shrink-wrap, dry cleaning bags, moisture barrier in construction, agricultural groundcover and greenhouse skins. LDPE can be drawn down to form very thin films that may be coated directly onto cardboard. The resulting product is a waterproof and heat-sealable composite that is widely used in juice and milk packaging. LDPE finds some minor applications in wire and cable insulation and flexible pipes. Injection- and blow-molded items made from LDPE are flexible and reasonably tough. Squeeze bottles and food storage containers are examples finished products. The rheological properties of molten LDPE make it suitable as a processing additive for other, less tractable PE grades.

<table>
<thead>
<tr>
<th>Application</th>
<th>Share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>65</td>
</tr>
<tr>
<td>Extrusion coating</td>
<td>10</td>
</tr>
<tr>
<td>Other extrusion</td>
<td>8</td>
</tr>
<tr>
<td>Injection molding</td>
<td>7</td>
</tr>
<tr>
<td>Blow molding</td>
<td>6</td>
</tr>
<tr>
<td>Others</td>
<td>4</td>
</tr>
</tbody>
</table>

2.3 HDPE and LLDPE

HDPE and LLDPE have very different properties. LLDPE is similar to LDPE and shares many applications with it, such as films. HDPE is the linear polyethylene suitable for molding applications (injection and blow). However, these two PE’s are made with coordination catalysts and their production processes share many common features. Coordination catalysts can control polymer microstructure much more efficiently than free radical initiators and are used to make polyethylene’s with a wide range of properties. There are basically four main types of olefin polymerization catalysts: 1) Ziegler-Natta catalysts; 2) Phillips catalysts; 3) metallocene catalysts; 4) late transition metals catalysts. Ziegler-Natta and Phillips catalysts were discovered in the early 1950’s, initiating a new era in olefin polymerization. The new generations of these catalysts are still leading the worldwide production of polyolefins. Metallocene and late transition metal catalysts were developed on the 1980s and 1990s, respectively. Metallocene catalysts are now exploited
industrially, the market share of metallocene PE’s is still relatively small but it is growing due to a particular combination of properties of metallocene PE’s respect to Ziegler-Natta and Phillips PE’s. Polymers made using late transition metals have had no significant commercial application to date. PE’s made with coordination catalysts generally have only SCB. Some specific metallocene or Phillips catalysts may be able to introduce some LCB but their LCB topology is different from that of LDPE. Ziegler-Natta catalysts can produce both HDPE and LLDPE. Phillips catalysts are very important for HDPE production, but are not used for LLDPE manufacture. Metallocene can be used in producing both HDPE and LLDPE, but as mentioned above, these products are very different from those produced with either Ziegler-Natta and Phillips catalysts.

Short chain branching in HDPE and LLDPE is produced by the copolymerization of \( \alpha \)-olefins added to the reactor as comonomers. This is schematically represented in the Figure 15, where Ti represent the catalyst active center.

Therefore, the higher the molar fraction of \( \alpha \)-olefin in the polymer chains, the higher is the number of SCB that act to reducing crystallinity and hence density. HDPE has a very low \( \alpha \)-olefin comonomer fraction (usually below a few mole percent). The comonomer content increases in LLDPE and with higher amount, very-low density and ultra-low density grades are produced. Density has been used for decades to classify polyethylene resins but this single parameter has some limitations. A better description of the polymer microstructure can be obtained by considering the chemical composition distribution (CCD) of LLDPEs, which describes the distribution of \( \alpha \)-olefin fraction in the polymer chains. Most commercial LLDPEs are made with heterogeneous Ziegler-Natta catalysts that have more than one type of active site. Each one is producing polymer chains with different average comonomer fractions and molecular weights. In addition, active sites that favor \( \alpha \)-olefin incorporation also favor lower average molecular weights. As a consequence, the
CCDs of Ziegler-Natta LLDPE resins are very broad, generally bimodal, and the average α-olefin content is correlated with polymer molecular weight. This is illustrated in the Figure 16.

![Figure 16. Branching distribution in linear polyethylenes as a function of feed composition (α-olefin)](image)

The low α-olefin part of the distribution appears as a sharp, high crystallinity peak. This is accompanied by a broad, low crystallinity peak at higher α-olefin content. As relative amount of polymers made by the two active sites changes, PE resins vary from HDPE with a unimodal, high-crystallinity peak (and sometimes a small lower crystallinity peak) to LLDPE with a more pronounced lower-crystallinity peak. Eventually, when the higher-crystallinity becomes very small, VLDPE and ULDPE are produced. The picture becomes even more complex when the joint distribution of molecular weight and chemical composition are considered in the same plot, as reported below for a Ziegler-Natta LLDPE. In this plot, CCD is combined with MWD and hence information about the distribution of α-olefin comonomer on chains of different length, i.e. molecular weight, is obtained.
PE pipes require very specific resin properties. Bimodal pipe resins have better mechanical properties if the higher molecular weight chains also have a higher $\alpha$-olefin fraction than the lower molecular weight component. The improved performance of bimodal resins have been linked to the presence of tie molecules, i.e. molecules linking crystalline and amorphous regions. With Ziegler-Natta catalyst, optimal properties of bimodal polyethylene’s for pipes cannot be obtained in a single reactor plant. Hence two or more reactors are used in series to produce the desired CCD x MWD combination. The first reactor makes low molecular weight HDPE in the absence, or very low concentration of $\alpha$-olefin, also using hydrogen as chain transfer agent to control molecular weight. The polymer produced in the first reactor is transferred continuously to the second reactor, which is operated under higher $\alpha$-olefin concentration in the absence, or under a much lower concentration of hydrogen, thus producing an LLDPE component with higher average molecular weight than the HDPE component made in the first reactor. Plant layout and a schematic representation of polymer properties are reported below.
The other very important class of heterogeneous catalysts for polyethylene production is the so-called “Phillips catalyst”. It is based chromium oxide grafted on a high-surface area amorphous support (usually porous silica). They were discovered by Hogan and Banks at the beginning in 1951 and first patented by Phillips. Today, Phillips catalyst are used almost exclusively for HDPE production and they account for about 40-45% of the global polyethylene production (Ziegler-Natta catalysts have an equivalent share, 45-50%). Metalloene catalysts have a much lower share, about 5% of the global volume).

The discovery of metalloene catalysts added a new dimension to commercial polyolefin resins. Metalloenes are single-site catalysts that make polyethylene’s with completely different microstructures from those made with Ziegler-Natta and Phillips catalysts. These PE are still classified as HDPE and LLDPE. Metalloene polyethylene’s (m-PE) have a uniform microstructure, with narrow MWD and CCD. Examples are given below for a series of ethylene/1-hexene copolymers made with a metalloene catalyst. All distributions are narrow and unimodal (the contrast with Ziegler-Natta LLDPE is well evident) with an uniform incorporation of 1-hexene and the absence of the high-crystallinity peak.
In conclusion, the main effect of catalyst class on MWD can be described by the following plot. It well evident that m-PEs have the narrower distribution, Ziegler-Natta PEs have intermediate values and Phillips catalysts have the wider.

The melt viscosity strongly depends on weight-average molecular weight and MWD. As reported below, samples made with different catalysts but with comparable weight-average molecular weight have very different flow curves. At very low frequency, Phillips PEs have higher viscosity, they do not show a Newtonian plateau and are highly shear-thinning. Metallocene PEs show a wide plateau
at low frequency and are much less shear sensitive. This is the reason why mPEs are sometimes
more difficult to process than other PEs. Ziegler-Natta PEs have some intermediate behavior.

![Viscosity](image)

**Figure 21. Effect of MWD on flow properties for the same polyethylene of Figure 20**

The three catalyst for PE production do not usually compete for the same application; instead each
serves a different part of market’s diverse needs.

Process technology for HDPE and LLDPE production relies on solution, slurry and gas phase,
processes. Slurry and solution technology were first introduced in mid 1950’s by Hoechst and
Phillips, respectively. Gas phase reactors arrived later, Union Carbide pioneered this technology
which was first industrially applied in 1968. A layout of a modern Chevron Phillips slurry plant is
reported below. Liquid isobutane is used to keep catalyst in suspension and the process runs under
mild conditions, 85 -105 °C and 42 bar. Ethylene (3 – 6 % concentration) is added along with 1-
hexene (or another α-olefin) and hydrogen to control molecular weight. Phillips and Ziegler-Natta
catalysts can be used,
Solution process is carried out at higher pressure and temperature, 30 -100 bar and 150 – 250 °C, respectively. Hence, the process has higher investment and operating cost. Cyclohexane is a typical solvent. Residence time in the reactor is short and both HDPE and LLDPE can be produced on the same plant. With cascade reactors, bimodal grades can be produced.
The gas phase or fluidized bed reactor technology operates under milder conditions, 70-110 °C and 15-30 bar. The reactions are slower, so long residence times are required. The investment and operating costs are low. This technology has bimodal capability with two or more reactors. HDPE and LLDPE can be produced on the same plant.
2.4 LLDPE

The ethylene/α-olefin copolymers cover a spectrum ranging from clear materials with stiffness similar to LDPE to rigid, opaque materials that share many of the characteristics of HDPE. Modulus determines resin suitability for a given application. Modulus depends on crystallinity which in turns is controlled by the level of comonomer and molecular weight. The majority of LLDPE resins have density values that fall within the range of LDPE, thus they share many of the same markets. Film production is the largest outlet for LLDPE, where its superior toughness gives benefits in terms of higher tear strength, impact resistance and puncture resistance. As an example, the properties of blown films produced using LDPE and LLDPE are reported in the table. For the same density and melt index, LLDPE films has better mechanical such as puncture resistance, tensile strength and elongation at break.
LLDPE films are used in many applications, including grocery sacks, fresh produce packages, stretch-wrap and domestic trash can liners. When the stiffness of HDPE is not required, LLDPE is a valid alternative for extrusion of wire and cable insulation, pipes and sheets. LLDPE can be also transformed by injection molding into such items as food container lids and toys, where flexibility combined with toughness is needed.

2.5 HDPE
HDPE macromolecules are essentially linear, with less than one branch per 200 carbon atoms in the backbone. As a consequence of chain linearity, high degrees of crystallinity are attained which result in the highest modulus and lowest permeability of all the classes of polyethylene. This combination of properties makes HDPE suitable for applications in certain medium- and large-scale liquid holders such as drums, tight-head pails and chemical storage tanks. On smaller scale items, a positive combination of stiffness, low permeability and high environmental stress cracking resistance, makes HDPE the first choice for bottles to contain household, industrial and automotive chemicals such as liquid detergents, bleach, motor oil and antifreeze liquids. The same properties are exploited in thin-walled food containers such as milk bottles and margarine tubs. Food packaging exposed to low temperature, for example freezer applications such as ice cream containers, are made out of HDPE which combines the low glass transition temperature of all polyethylene’s with the stiffness and strength required for containers. High crystallinity causes opacity and imparts a matte surface finish. This is a drawback of HDPE and for these reasons bottles and molded items are often pigmented to make them aesthetically more attractive. HDPE
has a good tensile strength that qualifies it for short-term load-bearing film applications such as grocery sacks, general merchandise bags and commercial trash liners. Its acceptable stiffness, durability and lightness make it suitable for a variety of household and commercial low-load-capacity applications, including crates, pallets and pails. Other domestic applications include pharmaceutical bottles, cosmetic containers and general storage containers. A good balance between toughness and rigidity make HDPE the resin of choice for many toys. Non-structural outdoor uses such as lawn furniture, playground equipments and trash can are other examples in which HDPE is selected because of a favorable balance between low glass transition temperature, satisfactory heat deflection temperature, reasonable stiffness and acceptable toughness. Very large parts such as municipal garbage cans, storage tank covers and canoes are produced with high density resins which have superior stiffness and a high abrasion resistance. HDPE resins are extruded to produce pipes for water, sewer and natural gas. In these applications, bimodal HDPE grades are specified as they offer the better combination of stiffness, low permeability and corrosion resistance.

HDPE thermo-mechanical properties need to be improved for some application where the service temperature exceeds the normal range for polyethylene. In hot water pipes, constant service temperatures up to 100 °C under load make standard HDPE not suitable. In electrical cable coating application, the temperature occasionally increases to such range as a consequence of a temporary overload. HDPE can be cross-linked to improve some mechanical and thermal properties. There are several technologies to crosslink PE at a specific stage of the production process. Radiation chemistry has been applied, by using electron beams on-line on the extrusion line or gamma radiation off-line. Radical initiators such as organic peroxides or azo compounds have also been exploited. Silane coupling dry or wet is another well known process.

The principal processing technologies for HDPE are molding, blow and injection. Extrusion find applications in pipes, wire and cable coating and sheet liners for liquid and solid waste contaminant pits.
Table 4. Correlation between properties and structural characteristic of polyethylenes

<table>
<thead>
<tr>
<th>Property</th>
<th>As Density Increases, Property:</th>
<th>As Melt Index Increases, Property:</th>
<th>As Molecular Weight Distribution Broadens, Property:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (At Yield)</td>
<td>Increases</td>
<td>Decreases</td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>Increases</td>
<td>Decreases Slightly</td>
<td>Decreases Slightly</td>
</tr>
<tr>
<td>Impact Strength</td>
<td>Decreases</td>
<td>Decreases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Low Temperature Brittleness</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>Increases</td>
<td>Decreases</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>Increases</td>
<td>Decreases Slightly</td>
<td></td>
</tr>
<tr>
<td>Softening Point</td>
<td>Increases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress Crack Resistance</td>
<td>Decreases</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Permeability</td>
<td>Decreases</td>
<td>Increases Slightly</td>
<td></td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Increases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Strength</td>
<td></td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Gloss</td>
<td>Increases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haze</td>
<td>Decreases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shrinkage</td>
<td>Decreases</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Overall comparison of properties for the three main PE’s

<table>
<thead>
<tr>
<th>Property</th>
<th>HDPE</th>
<th>LDPE</th>
<th>LLDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm⁻³)</td>
<td>0.94 – 0.97</td>
<td>0.91 – 0.94</td>
<td>0.90 – 0.94</td>
</tr>
<tr>
<td>Degree of crystallinity (% from density)</td>
<td>62 – 82</td>
<td>42 – 62</td>
<td>34 – 62</td>
</tr>
<tr>
<td>Degree of crystallinity (% from calorimetry)</td>
<td>55 – 77</td>
<td>30 – 54</td>
<td>22 – 55</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>1000 - 1500</td>
<td>240 - 330</td>
<td>280 - 1100</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>1100 - 1400</td>
<td>170 - 350</td>
<td>260 - 900</td>
</tr>
<tr>
<td>Tensile yield stress (MPa)</td>
<td>18 – 31</td>
<td>9 – 19</td>
<td>8 – 19</td>
</tr>
<tr>
<td>Tensile strength at break (MPa)</td>
<td>22 - 31</td>
<td>8 - 31</td>
<td>13 - 45</td>
</tr>
<tr>
<td>Tensile elongation at break (%)</td>
<td>10 - 1500</td>
<td>100 – 650</td>
<td>100 - 950</td>
</tr>
<tr>
<td>Shore hardness (D)</td>
<td>66 – 73</td>
<td>44 – 50</td>
<td>55 - 70</td>
</tr>
<tr>
<td>Izod impact strength, notched (J/cm)</td>
<td>0.21 – 2.13</td>
<td>no break</td>
<td>0.19 – no break</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>125 – 132</td>
<td>98 – 115</td>
<td>100 - 125</td>
</tr>
<tr>
<td>Heat distortion temperature (°C, @ 0.45 MPa)</td>
<td>80 - 90</td>
<td>40 – 44</td>
<td>55 - 80</td>
</tr>
<tr>
<td>Heat of fusion (J/g)</td>
<td>138.1 – 221.8</td>
<td>87.9 – 154.8</td>
<td>62.8 – 179.9</td>
</tr>
<tr>
<td>Thermal expansivity (10⁻⁶ cm/cm/°C)</td>
<td>60 – 110</td>
<td>100 – 220</td>
<td>70 - 150</td>
</tr>
</tbody>
</table>

2.6 POLYPROPYLENE

The global polypropylene (PP) market is the second largest volume polymer business in the world today making up 25% of global polymer demand. The global demand for PP attained 58 million metric ton in 2013 and is expected to grow up to 68 million metric tons in 2016. Global demand growth continues to be led by emerging economies, especially China where major investments in new capacity attempt to improve China’s self-sufficiency. Unconventional low cost feedstocks are driving new capacity investment in North America (shale gas) and China (coal) and will have significant effects on future global trade and regional competitiveness. Less competitive regions will have to adapt through supply rationalizations or with new product and process innovations.

PP is prepared by propylene polymerization in the presence of a catalyst under carefully controlled temperature and pressure. Propylene is an unsaturated hydrocarbon and during polymerization the double bond reacts forming new carbon-carbon single bonds that keep monomer units together.
Many propylene molecules are joined together to form large PP molecules according to the following scheme.

Here M* represents an organometallic, transition metal catalyst that provide a site for the reaction to occur. Propylene molecules are added sequentially through a reaction between the metallic function group of the growing polymer chain and the double bond of the propylene monomer. A long, linear polymer chain of carbon atoms is formed, with methyl groups (CH₃) attached to every other carbon atom of the chain.

Widely used catalysts in industry are based on a complex of transition metals halides (such as TiCl₃) with an organometallic compound, in most cases triethylaluminum. The complex is supported on MgCl₂, for example, giving rise to the well-known Ziegler-Natta catalysts from the names of the two independent inventors. The catalysts, developed originally in the late ‘50s, have evolved through different generations with ever increasing productivity (kg of polymer produced
per gram of metal). They are sometimes referred to as “multi-site” catalyst as they contain several reactive sites (of different reactivity).

More recently, new catalysts for PP production have been introduced at the industrial scale. The new catalysts are based on organometallic compounds with a sandwich-like structure in which the metal atom (Zr, Ti, and Fe) is located between two molecules of a cyclic organic compounds. Such a complex is called a metallocene. Propylene molecules during polymerization are inserted on a metal-carbon bond in the complex and for this reason every complex has the same reactivity. This is why such catalysts are often referred to as “single site” catalysts.

Figure 25. Metallocene catalyst

For large-scale industrial production, the metallocene must be fixed on a powdery, insoluble substrate like Al₂O₃ or MgCl₂. Active sites on each grain are identical and PP chains growing from the surface have a more uniform length.

Either with Ziegler-Natta and metallocene catalysts, the polymerization reaction is highly stereospecific. The chemical and the crystal structure of the catalyst control the orientation of the propylene molecules while they are inserted on the growing chain. This control ensures a highly stereospecific polymerization reaction. As reported in the scheme below, propylene molecules are added head-to-tail and not head-to-head or tail-to-tail.
Head-to-tail addition leads to a polypropylene chain with pendant methyl groups attached to alternating carbon atoms. Head-to-head or tail-to-tail addition disrupts this alternating arrangement. Polypropylene can be isotactic, syndiotactic or atactic, depending on the orientation of the pendant methyl groups. The three different arrangements are described schematically below.

Isotactic polypropylene is the most common commercial form. Pendant methyl groups are all in the same configuration and are on the same side of the polymer chain. As a result of this regular, repeating arrangement, isotactic PP has a high degree of crystallinity. In syndiotactic PP, alternate pendant methyl groups are on opposite sides of the polymer backbone, with exactly opposite configuration relative to the polymer chain. Syndiotactic PP can be produced by metalloocene catalysts and it is still able to crystallize. In atactic PP, pendant methyl groups have a random orientation with respect to the polymer backbone. This disordered orientation inhibits crystallization and hence atactic PP has a very low crystallinity, if any. Catalyst used and polymerization
conditions control the relative amount of isotactic, syndiotactic and atactic segments in the PP chains.

Isotactic PP has the highest crystallinity that provides good mechanical properties such as stiffness and tensile strength. Syndiotactic PP is less stiff than isotactic, but has better impact strength and clarity. As an outcome of its irregular structure, atactic PP has very low crystallinity, resulting in a sticky, amorphous material with poor mechanical properties but useful in formulations such as some adhesives and roofing tars. Catalyst properties and process parameters are used to control the relative amount of isotactic and atactic PP in commercial grades. The isotactic content is expressed as a tacticity index that can be measured with 13-carbon nuclear magnetic resonance spectroscopy. The amount of atactic PP in commercial grades is often determined by extraction with xylene, in which only atactic PP is soluble at room temperature. Levels of atactic PP range from about 1-20%. The table 6 reports a synthesis of the effect of atactic PP on commercial PP grade properties.

Molecular weight is an important parameter to characterize a polymer material. The range of molecular weights for commercial PP is $M_n = 38,000$ to $60,000$ and $M_w = 220,000$ to $700,000$.

Another widely used parameter to characterize a polymer compound is the melt flow index (MFI). For commercial PP grades, MFI can be as low as 0.3 g/10 min up to 1800 g/10 min for some of the new metallocene grades (m-PP). There is an inverse relationship between MFI and molecular weight. A high molecular weight grade has low melt index and vice versa.

High viscosity grades with low MFI, usually less than 2, are suitable for extrusion processes, such as sheet and blow molding. These grades have the high melt strength required by such processes. Intermediate MFI grades, in the range 2 – 8 for example, are used in film and fiber application. Materials with MFI values of 8 – 35 or more are used in extrusion coating, injection molding of thin-walled parts that require rapid filling and also in fiber spinning. The effect of molecular weight on PP properties is summarized in the table below.
Table 6. Effect of atacticity on polypropylene properties

<table>
<thead>
<tr>
<th>Property</th>
<th>With Increasing Atacticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stiffness</td>
<td>Decreases</td>
</tr>
<tr>
<td>Moduli</td>
<td>Decrease</td>
</tr>
<tr>
<td>Strength</td>
<td>Decreases</td>
</tr>
<tr>
<td>Room Temperature Impact Resistance</td>
<td>Increases</td>
</tr>
<tr>
<td>Stretchability</td>
<td>Increases</td>
</tr>
<tr>
<td>Elongation</td>
<td>Increases</td>
</tr>
<tr>
<td>Shear Rheology</td>
<td>Increases</td>
</tr>
<tr>
<td>Long Term Heat Aging (LTHA) Resistance</td>
<td>Decreases</td>
</tr>
<tr>
<td>Heat Distortion Temperature</td>
<td>Decreases</td>
</tr>
<tr>
<td>Heat Seal Strength</td>
<td>Increases</td>
</tr>
<tr>
<td>Haze in Films</td>
<td>Decreases</td>
</tr>
<tr>
<td>Blocking in Films</td>
<td>Increases</td>
</tr>
<tr>
<td>Irradiation Tolerance</td>
<td>Increases</td>
</tr>
<tr>
<td>Extractables (solubility)</td>
<td>Increase</td>
</tr>
<tr>
<td>Smoke and Fume Generation</td>
<td>Increases</td>
</tr>
<tr>
<td>Color Quality</td>
<td>Decreases</td>
</tr>
<tr>
<td>General Optical Properties</td>
<td>Increase</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>Decreases</td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>Decreases</td>
</tr>
<tr>
<td>Crystallization Temperature</td>
<td>Decreases</td>
</tr>
</tbody>
</table>
The toughness of a PP grade is directly related to molecular weight: higher molecular weights provide greater toughness. As a result, higher molecular weight PP have greater impact resistance and elongation and less brittleness. However, other properties are affected in the opposite direction. Elastic modulus, for example, and thermo mechanical properties such as heat deflection temperature decrease with increasing molecular weight, in part as a consequence of lower crystallinity of high molecular weight grades.

In addition to molecular weight and MFI, the molecular weight distribution MWD, (Mw/Mn) is another very important parameter characterizing any polymer materials. For commercial PP grades, MWD can range from 2 to 11. A narrow MWD means that most polymer chains have approximately the same length, whereas in broad MWD chains vary widely in length. In particular, there are a few very short chains and a few very long chains. MWD influences the processability of a resin due to the shear sensitivity of molten PP. Being non-Newtonian fluids, polymer melts show shear thinning behavior, that is apparent viscosity decreasing with increasing
shear rate. As reported in the Figure below, a PP sample with a broad MWD is more shear sensitive than a PP sample with a narrow MWD.

![Log Viscosity (Poise) vs Log Shear Rate (Sec^-1)](image)

**A. Broad Molecular Weight Distribution**

**B. Narrow Molecular Weight Distribution**

As a consequence, PP grades with a broad MWD are processed more easily by injection molding. PP grades with narrow MWD are better used in extrusion, where a narrower MWD generally ensures a higher achievable extrusion output rate. Fiber spinning is another application where a narrow MWD is preferred.

The market success and expansion of PP were driven by the development of new generation catalysts. The manufacturing processes followed catalysts evolution and became simpler and more efficient. A block diagram of a solvent-based polymerization process using first generation Ziegler-Natta catalyst is reported below. Catalyst granules were suspended in an inert solvent like hexane or heptane, which was recovered and recycled after the polymerization. PP produced contained about 10% by weight of atactic polymer, a fraction too high for the desired polymer properties. Purification steps to remove the atactic fraction by solvent extraction were mandatory. In addition, catalyst residue concentration was too high because of low PP yields (expressed as kg of polymer produced per gram of catalyst). These residues had to be extracted by water and alcohol extraction (deashing step) from the PP produced.
In the second generation processes, the improved catalyst efficiency allowed for the elimination of deashing. In this way, the large amount of alcohol and water became unnecessary and the production cost was significantly reduced. The new catalysts also opened up the opportunity for a new non-solvent polymerization technology in which the catalyst particles were suspended in liquid monomer without the need of a solvent. However, the atactic fraction was still too high in the second generation processes and solvent extraction was needed in both solvent and bulk polymerization plants.
Several improvements introduced on catalyst formulation and production led to the elimination of atactic polymer extraction when the third generation processes went on stream. The process layout became very simple, as downstream to polymerization reactor PP is separated from residual monomer which is recycled back to the polymerization reactor. The third generation catalysts, for
which deashing and atactic PP extraction were not required, were applied in gas phase propylene polymerization. Propylene monomer is polymerized under milder conditions from the gas phase on the surface of solid catalyst particles. This option, originally pioneered with the first generation Ziegler Natta catalyst, could not be applied at that time because atactic removal and deashing were mandatory.

![Figure 31. Block diagram of a third generation polypropylene plant](image1)

The catalysts of later generations (from third generation onward) are active also in propylene copolymerization with other olefins such as ethylene, 1-butene and 1-hexene. Two new families of polypropylene based materials were then introduced on the market: random and impact copolymers. Random copolymers are produced in the same reactor to which propylene with a small amount of another olefin is fed (usually a few percent, 1 – 7 weight percent of ethylene). Impact copolymers contain a much higher concentration of ethylene or other α-olefins and the production process requires at least two reactors in series. In the first, propylene in polymerized and the particles are transferred to a second reactor where new propylene along with ethylene is fed.

![Figure 32. Layout of an ethylene-propylene copolymer plant](image2)

3. POLYAMIDES
3.1 Introduction

Polyamides are polymers which contain repeating amide (-CO-NH-) linkages. Proteins are examples of naturally occurring polyamides. Aliphatic polyamides with linear alkyl chains are also known as Nylon, that is the trade name given by DuPont in 1939 that has first commercialized Nylon fibers. Indeed Nylon was developed in the 1930s by scientists at Du Pont, headed by an American chemist Wallace Hume Carothers (1896-1937). The versatility of Nylons makes them the most widely used engineering thermoplastics. Polyamides have excellent mechanical properties and can be either hard and tough or soft and flexible. They absorb moisture and have excellent slide and wear characteristics. Polyamides are commonly used in the textile and automotive industries.

3.2 Different types of polyamides

Polyamides can have different length of alkylene chains and different sequences and orientations of amide groups. The properties of the polyamide strongly depend on the density of the strong polar amide groups that is connected to the chain length of the aliphatic linear chain.

The names of nylons are related to the number of carbon atoms between two nitrogen atoms in the polymer chain. If the polyamide is obtained from an α-ω aminoacid or from a lactam only a number is given in the name of the nylon (e.g. Nylon 6 from caprolactam or nylon 11 form amino-undecanoic acid) while a double number is given if the nylon comes from the reaction of a diacid with a diamine.
<table>
<thead>
<tr>
<th>Polyamide</th>
<th>Repeating unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6</td>
<td><img src="image" alt="Nylon 6 Repeating Unit" /></td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td><img src="image" alt="Nylon 6,6 Repeating Unit" /></td>
</tr>
<tr>
<td>Nylon 6,10</td>
<td><img src="image" alt="Nylon 6,10 Repeating Unit" /></td>
</tr>
<tr>
<td>Nylon 11</td>
<td><img src="image" alt="Nylon 11 Repeating Unit" /></td>
</tr>
<tr>
<td>Nylon 12</td>
<td><img src="image" alt="Nylon 12 Repeating Unit" /></td>
</tr>
</tbody>
</table>

Figure 33. Chemical structure of the most important aliphatic polyamides
3.3 Polyamides market

Polyamides are widely used as thermoplastic materials and as fibers with an increasing growth of production (Figure 34).

Germany is the European country with the highest use, followed by Italy and France (Figure 35).
Among polyamides, Nylon 6 and Nylon 6,6 cover almost the 95% of Nylon market with similar market shares (Figure 36). Longer alkyl chain Nylons are more expensive and are used in more specific applications.

Figure 35. Polyamide use by country (data from British Plastic Federation).

Figure 36. Polyamide use by material type (data from British Plastic Federation)
The main application area of Nylons is the automotive industry, followed by electrical and electronics and packaging (Figure 37). World consumption of Nylon 6 and Nylon 6,6 are shown in Figure 38 and Figure 39, respectively (data refer to 2013). China has become the main consumer of both Nylons. China’s Nylon consumption breakdown by process/market segment shows a pattern common to Western countries (see Figure 40).

Figure 37. Polyamide use by application area (data from British Plastic Federation)

Figure 38. World consumption of nylon 6 (2013)
Figure 39. World consumption of nylon 6-6 (2013)

Figure 40. China’s nylon consumption (2012)
3.4 Polyamides synthesis

Both polyamides 6 and 6,6 are manufactured from benzene via cyclohexane. Hydrogen is passed through liquid benzene in the presence of a nickel catalyst under pressure to produce cyclohexane (Figure 41).

\[
\text{benzene} + 3\text{H}_2 \xrightarrow{\text{Nickel catalyst, 450 K, 40 atm}} \text{cyclohexane}
\]

Figure 41. Cyclohexane synthesis

Cyclohexane is oxidized by passing air through the liquid under pressure in the presence of a catalyst (often a cobalt salt) to yield two products: cyclohexanol and cyclohexanone (Figure 42).

The mixture of cyclohexanol and cyclohexanone is also known as "mixed oil" or KA (ketone/alcohol).

An alternative route to cyclohexanol is via the hydrogenation of phenol using a nickel catalyst at approx. 130°C and 5 atm (Figure 43).
A more recent route to cyclohexanol is the Asahi process from benzene via its hydrogenation to cyclohexene and subsequent hydration to alcohol. This is more energy efficient than the other processes.

To make polyamide 6, pure cyclohexanone is required. When the mixed oil is heated under pressure with copper(II) and chromium(III) oxides, the cyclohexanol, which is a secondary alcohol, is dehydrogenated to the corresponding ketone, cyclohexanone (Figure 44).

Cyclohexanone is then converted into caprolactam via the oxime (produced by the reaction of the ketone with hydroxylamine - in the form of the salt, hydroxylamine hydrogensulfate) (Figure 45).
The isomerisation of the oxime to caprolactam by sulfuric acid is an example of the Beckmann rearrangement in which an oxime is transformed into an amide in the presence of acid. A zeolite, with acidic sites, is also being used to effect the rearrangement. The zeolite is regenerated and saves the use of sulfuric acid. To produce the polymer, the caprolactam, water (acting as a catalyst) and a molecular mass regulator, e.g. ethanoic acid, are poured into a reaction vessel and heated under nitrogen at 230 °C for about 12 hours (Figure 46).

![Figure 46. Caprolactam polymerization](image)

Polyamide 6,6 is produced by reacting 1,6-diaminohexane (hexamethylenediamine) with hexanedioic acid (adipic acid) by condensation polymerization. One of the monomers, hexanedioic acid is also produced from KA mixed oil (cyclohexanol and cyclohexanone). The mixed oil is oxidized in the liquid phase using moderately concentrated (60%) nitric acid and a copper(II) nitrate and ammonium vanadate(V) catalyst, at 60°C to form hexanedioic acid (Figure 47).

![Figure 47. Hexanedioic acid](image)

This process has a considerable disadvantage. A side-product is nitrogen(I) oxide (nitrous oxide), N₂O (a powerful greenhouse) gas but it is carefully removed by thermal or catalytic treatment units. The second monomer, 1,6-diaminohexane, is produced from 1,3-butadiene and from propenonitrile (polyacrylonitrile).
To form the polymer, the acid and the diamine are then heated together to form a salt. The chemical reaction for aliphatic dicarboxylic acids and aliphatic diamines to yield an aliphatic polyamide via a condensation polymerization process is represented in Figure 48.

![Figure 48. Diacid and diamine polycondensation](image)

The chain length is regulated by controlling process conditions, such as reaction time, temperature and pressure. An aqueous solution of the salt is heated, in the absence of air, to ca 230°C. A pressure develops in the vessel, the temperature is then raised to 270°C and the steam is bled off to keep the pressure constant. Eventually, the pressure is reduced and the polymer is extruded under nitrogen to yield a lace which is then granulated.

### 3.5 Properties

Both nylon 6 and nylon 6,6 are semi-crystalline polymers. These linear aliphatic polyamides are able to crystallize mostly because of strong intermolecular hydrogen bonds through the amide groups and because of Van der Waals forces between the methylene chains. Since these unique structural and thermo-mechanical properties ofnylons are dominated by the hydrogen bonds in these polyamides, quantum chemistry can be used to determine the hydrogen bond potential. The
left side of Figure 47 shows hydrogen-bonding planes, and the right side shows the view down the chain axis. For the $\alpha$-form of nylon 6, adjacent chains are antiparallel and the hydrogen bonding is between adjacent chains within the same sheet (bisecting the CH$_2$ angles). For the $\gamma$-form of nylon 6, the chains are parallel and the hydrogen bonding is between chains in adjacent sheets. In nylon 6,6, the chains have no directionality. Research results have shown that the stable crystalline structure is the $\alpha$-form comprised of stacks of planar sheets of hydrogen-bonded extended chains. It also appears that Young's modulus of the $\alpha$-form is higher than the $\gamma$-form.

Figure 49. Crystal structures of Nylon 6 and 6,6

Mechanical, thermal and optical properties of fibers are strongly affected by orientation and crystallinity. Basically, higher fiber orientation and crystallinity will produce better properties.
Crystallinity of nylons can be controlled by nucleation, i.e., seeding the molten polymer to produce uniform sized smaller spherulites. This results in increased tensile yield strength, flexural modulus, creep resistance, and hardness, but some loss in elongation and impact resistance. Another important benefit obtained from nucleation is decrease of setup time during processing.

The Heat distortion temperature (HDT) and melting temperature depend on the hydrogen bonding due to the amide groups. Therefore, polyamides with shorter alkyl chains present higher melting temperatures and HDT. Nylon 6,6 present an higher melting temperature and HDT compared to nylon 6 due to the more efficient formation of hydrogen bonding between polymer chains.

![Figure 50. HDT (measured at 0.45 MPa load) and melting temperature of most important polyamides](image)

The density of long chain polyamides (12 and 11) is lower to that of nylons with short alkyl chains (6 and 6,6) due to a less strong packing caused by the lower interaction between chains.
Polyamides have a strong water uptake due to the presence of the polar amide groups. The polyamides with higher amide groups density (PA 6 and PA 6,6) have the highest moisture and water uptake.

The mechanical properties of polyamides are strongly influenced by water adsorption in particular.
for PA 6 and PA 6,6. In particular, the tensile stress is reduced to less than half for PA 6,6 after conditioning with a relative humidity of 50%. Long alkyl chain polyamides (PA 11 and 12) are less susceptible to change in mechanical properties after water adsorption.

Figure 53. Tensile stress at yield after and before conditioning, measured by ISO 527

The impact resistance (measured by notched Charpy) of polyamides with short chains is good at room temperature, but significantly decreases at low temperature. Long alkyl chain polyamides (in particular Nylon 11) present the best performances in terms of impact resistance at low temperatures and for this reason are for example used in winter sport equipments.
The resistance to solvents, acid and bases depends on the length of alkyl chains (Table 9). Nylons with longer alkyl chain have a more hydrophobic behavior and are less resistant to solvent exposures.

Table 8. Solvent resistance of polyamides

<table>
<thead>
<tr>
<th></th>
<th>Acetic Acid</th>
<th>Nitric Acid</th>
<th>Sulfuric Acid</th>
<th>Glycol</th>
<th>Zinc Chloride</th>
<th>Calcium Hydroxide</th>
<th>Toluene</th>
<th>Alcohols</th>
<th>Fuels</th>
<th>Calcium Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radilon A – PA66</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>P</td>
<td>F</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Radilon S – PA6</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Radilon D – PA6.10</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>PA11</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>E</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>PA12</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>E</td>
<td>F</td>
<td>G</td>
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<td>E</td>
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<tr>
<td>PA6.12</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>E</td>
</tr>
</tbody>
</table>

E = excellent, G = Good, F = Fair, P = Poor
3.6 Polyamides from renewable resources

Monomers for polyamides can be obtained using renewable feedstocks. In particular the cracking reaction of castor oil has been used since 1947 for the synthesis of 11-aminoundecanoic acid by Arkema. The steps for the preparation of aminoundecanoic acid from castor oil are presented in Figure 55.

The cracking reaction can also be used for the preparation of sebacic acid used for the synthesis of Nylon 6,10 that in this way is composed of 64% by weight of materials deriving from renewable resources (Figure 56).
The use of renewable feedstocks reduces the carbon footprint of the material and have a positive effect on the global warming (Figure 57).
The bioplastic market and in particular the market of polymers from renewable resources is actually less than 1% of the global plastic market with a total production of 1395 kton/year in 2012 but with an exponential increase with a prediction of 6185 kton/y in 2017 (Figure 58).

At the moment the amount of polyamides made from renewable resources is of 2.4% of the total amount of bioplastics (Figure 59).
Figure 59. Bioplastic production capacities by material type in 2012 (source European Bioplastic Association)
4. POLYLACTIC ACID

Polylactic acid (PLA) is at present one of the most promising biodegradable polymers (biopolymers) and has been the subject of abundant literature over the last decade. PLA can be processed with a large number of techniques and is commercially available (large-scale production) in a wide range of grades. It is relatively cheap and has some remarkable properties, which make it suitable for different applications. This chapter deals with the different syntheses to produce this biopolymer, its diverse properties and various applications. Its biodegradability is adapted to short-term packaging, and its biocompatibility in contact with living tissues is exploited for biomedical applications (implants, sutures, drug encapsulation ...).

4.1 Introduction

Tailoring new materials within a perspective of eco-design or sustainable development is a philosophy that is applied to more and more materials. It is the reason why material components such as biodegradable polymers can be considered as ‘interesting’ – environmentally safe – alternatives. Besides, ecological concerns have resulted in a resumed interest in renewable resources-based products. Figure 58 shows an attempt to classify the biodegradable polymers into two groups and four different families. The main groups are (i) the agro-polymers (polysaccharides, proteins, etc.) and (ii) the biopolysteres (biodegradable polyesters) such as polylactic acid (PLA), polyhydroxyalkanoate (PHA), aromatic and aliphatic copolyesters. Biodegradable polymers show a large range of properties and can now compete with non-biodegradable thermoplastics in different fields (packaging, textile, biomedical, etc.). Among these biopolysteres, PLA is at present one of the most promising biopolymer. PLA can be processed with a large number of techniques. PLA is commercially and largely available (large-scale production) in a wide range of grades. It has a reasonable price and some remarkable properties to fulfill different applications. For instance, the PLA production capacity of Cargill (USA) in 2006 was 140 kT per year at 2–5 Euros per kg. Other companies, such as Mitsui Chemical (Lacea-Japan), Treofan (Netherland), Galactic (Belgium), Shimadzu Corporation (Japan), produce smaller quantities. Some of them are only focused on the biomedical market like Boeringher Ingelheim (Germany), Purac (Netherland) or Phusis (France), because the constraints of this market are very specific. However, according to different sources, PLA consumption in 2006 was only about 60.000 tons per year and, at present, only 30% of lactic acid is used for PLA production. Thus, this biopolymer presents a high potential for development.
PLA belongs to the family of aliphatic polyesters commonly made from \( \alpha \)-hydroxy acids, which also includes, for example, polyglycolic acid (PGA). It is one of the few polymers in which the stereochemical structure can easily be modified by polymerizing a controlled mixture of L and D isomers (Figure 59) to yield high molecular weight and amorphous or semi-crystalline polymers. Properties can be both modified through the variation of isomers (l/d ratio) and the homo and (D, L) copolymers relative contents. Besides, PLA can be tailored by formulation involving adding plasticizers, other biopolymers, fillers, etc. PLA is considered both as biodegradable (e.g. adapted for short-term packaging) and as biocompatible in contact with living tissues (e.g. for biomedical applications such as implants, sutures, drug encapsulation, etc.). PLA can be degraded by abiotic degradation (i.e. simple hydrolysis of the ester bond without requiring the presence of enzymes to catalyze it). During the biodegradation process, and only in a second step, the enzymes degrade the residual oligomers till final mineralization (biotic degradation). As long as the basic monomers (lactic acid) are produced from renewable resources (carbohydrates) by fermentation, PLA complies with the rising worldwide concept of sustainable development and is classified as an environmentally friendly material.

4.2 Synthesis of PLA
The synthesis of PLA is a multistep process which starts from the production of lactic acid and ends with its polymerization. An intermediate step is often the formation of the lactide. Figure 2 shows that the synthesis of PLA can follow three main routes. Lactic acid is condensation polymerized to yield a low molecular weight, brittle polymer, which, for the most part, is unusable, unless external coupling agents are employed to increase its chains length. Second route is the azeotropic dehydrative condensation of lactic acid. It can yield high molecular weight PLA without the use of chain extenders or special adjuvants. The third and main process is ring-opening polymerization (ROP) of lactide to obtain high molecular weight PLA, patented by Cargill (US) in 1992. Finally, lactic acid units can be part of a more complex macromolecular architecture as in copolymers.

**Figure 61. Synthesis methods for obtaining high molecular weight PLA.**

### 4.2.1 Precursors

**Lactic acid**

Lactic acid is a compound that plays a key role in several biochemical processes. For instance, lactate is constantly produced and eliminated during normal metabolism and physical exercise. Lactic acid has been produced on an industrial scale since the end of the nineteenth century and is...
mainly used in the food industry to act, for example, as an acidity regulator, but also in cosmetics, pharmaceuticals and animal feed. It is, additionally, the monomeric precursor of PLA. It can be obtained either by carbohydrate fermentation or by common chemical synthesis. Also known as ‘milk acid’, lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom and two optically active configurations, namely the L and D isomers (Figure 61), which can be produced in bacterial systems, whereas mammalian organisms only produce the L isomer, which is easily assimilated during metabolism. Lactic acid is mainly prepared in large quantities (around 200 kt per year) by the bacterial fermentation of carbohydrates. These fermentation processes can be classified according to the type of bacteria used: (i) the hetero-fermentative method, which produces less than 1.8 mol of lactic acid per mole of hexose, with other metabolites in significant quantities, such as acetic acid, ethanol, glycerol, mannitol and carbon dioxide; (ii) the homo-fermentative method, which leads to greater yields of lactic acid and lower levels of by-products, and is mainly used in industrial processes. The conversion yield from glucose to lactic acid is more than 90 %. The majority of the fermentation processes use species of Lactobacilli which give high yields of lactic acid. Some organisms predominantly produce the L isomer, such as Lactobacilli amylophilus, L. bavaricus, L. casei and L. maltaromicus, whereas, L. delbrueckii, L. jensenii or L. acidophilus produce the D isomer or a mixture of L and D. These different bacteria are homo-fermentative. In general, the sources of basic sugars are glucose and maltose from corn or potato, sucrose from cane or beet sugar, etc. In addition to carbohydrates, other products, such as B vitamins, amino acids and different nucleotides, are formed. The processing conditions are an acid pH close to 6, a temperature around 40°C and a low oxygen concentration. The major method of separation consists in adding CaCO3, Ca(OH)2, Mg(OH)2, NaOH, or NH4OH to neutralize the fermentation acid and to give soluble lactate solutions, which are filtered to remove both the cells (biomass) and the insoluble products. The product is then evaporated, crystallized, and acidified with sulphuric acid to obtain the crude lactic acid. If the lactic acid is used in pharmaceutical and food applications, it is further purified to remove the residual by-products. If it is to be polymerized, it is purified by separation techniques including ultra-filtration, nano-filtration, electro-dialysis and ion-exchange processes.

**Lactide**
Figure 62 shows the different stereo-forms of lactide. The cyclic dimer of lactic acid combines two of its molecules and gives rise to L-lactide or LL-lactide, D-lactide or DD-lactide, and meso-lactide or LD-lactide (a molecule of L-lactic acid associated with another one of D-lactic acid). A mixture of L- and D- lactides is a racemic lactide. Lactide is usually obtained by the depolymerization of low molecular weight PLA under reduced pressure to give a mixture of L-, D- and meso-lactides. The different percentages of the lactide isomers formed depend on the lactic acid isomer feedstock, temperature and the catalyst’s nature and content. A key point in most of the processes is the separation between each stereoisomer to control the final PLA structure (e.g. by vacuum distillation) which is based on the boiling point differences between the meso- and the L- or D-lactide.

![Chemical structure of L-, meso- and D- lactides](image)

**Figure 62. Chemical structure of L-, meso- and D- lactides**

### 4.2.2 PLA polymerization

**Lactic acid condensation and coupling**

The condensation polymerization is the least expensive route, but it is difficult to obtain high molecular weights by this method. The use of coupling or esterification promoting agents is required to increase the chains length, but at the expense of an increase in both cost and complexity (multistep process). The role of chain coupling agents is to react with either the hydroxyl (OH) or the carboxyl end-groups of the PLA thus giving telechelic polymers. The nature of the chain end-groups should be fully controlled. The use of chain-extending agents brings some advantages, because reactions involving small amounts of them are economical and can be carried out in the melt without the need of separating the different process steps. The tunability to design copolymers with various functional groups is also greatly expanded. The disadvantages are that the final
polymer may contain unreacted chain extending agents, oligomers and residual metallic impurities from the catalyst. Moreover, some extending agents could be associated with a lack of biodegradability. Examples of chain-extending agents are anhydrides, epoxides and isocyanates. Similar products are used to develop compatibilization for PLA-based blends. The disadvantages of using isocyanates as chain extenders are their (eco)toxicity.

The advantages of esterification promoting adjuvants are that the final product is highly purified and free from residual catalysts and/or oligomers. The disadvantages are higher costs due to the number of steps involved and the additional purification of the residual by-products, since these additives produce by-products that must be neutralized or removed.

**Azeotropic dehydration and condensation**

The azeotropic condensation polymerization is a method used to obtain high chain lengths without the use of chain extenders or adjuvants and their associated drawbacks. Mitsui Chemicals (Japan) has commercialized a process wherein lactic acid and a catalyst are azeotropically dehydrated in a refluxing, high boiling, aprotic solvent under reduced pressures to obtain high molecular weight PLA (Mw $\geq$ 300,000). A general procedure consists in the reduced pressure distillation of lactic acid for 2–3 h at 130°C to remove most of the condensation water. The catalyst and diphenyl ether are then added and a tube packed with molecular sieves is attached to the reaction vessel. The refluxing solvent is returned to the vessel by way of the molecular sieves during 30–40 h at 130°C. Finally, the ensuing PLA is purified. This polymerization gives considerable catalyst residues because of its high concentration needed to reach an adequate reaction rate. This can cause many drawbacks during processing, such as degradation and hydrolysis. For most biomedical applications, the catalyst toxicity is a highly sensitive issue. The catalyst can be deactivated by the adding of phosphoric acid or can be precipitated and filtered out by the addition of strong acids such as sulphuric acid. Thus, residual catalyst contents can be reduced to some ppm.

**ROP of lactide**

The lactide method is the only method for producing pure high molecular weight PLA (Mw $\geq$ 100,000). The ROP of lactide was first demonstrated by Carothers in 1932, but high molecular weights were not obtained until improved lactide purification techniques were developed by DuPont in 1954. This polymerization has been successfully carried out calling upon various methods, such as
solution, bulk, melt or suspension process. The mechanism involved in ROP can be ionic (anionic or cationic) or coordination–insertion, depending on the catalytic system. The role of the racemization and the extent of transesterification in the homo or copolymerization, are also decisive for the enantiomeric purity and chain architecture of the resulting macromolecules. It has been found that trifluoromethane sulphonic acid and its methyl ester are the only cationic initiators known to polymerize lactide, and the mechanism of this process has been outlined in different papers.

Lactide anionic polymerizations proceed by the nucleophilic reaction of the anion with the carbonyl group and the subsequent acyl–oxygen bond cleavage, which produces an alkoxide end-group, which continues to propagate. The general mechanism for this anionic polymerization has been discussed in various publications. Some authors have shown that the use of alkoxides, such as potassium methoxide, can yield well defined polymers with negligible racemization.

![Figure 63. ROP by the cationic mechanism](image)

![Figure 64. ROP by the anionic mechanism](image)
Both the anionic and cationic ROPs (Figure 63 and 64, respectively) are usually carried out in highly purified solvents, and although they show a high reactivity, they are susceptible to give racemization, transesterification and high impurity levels. For industrial and large commercial use, it is preferable to do bulk and melt polymerization with low levels of non-toxic catalysts. The use of less-reactive metal carboxylates, oxides and alkoxides has been extensively studied in this context, and it has been found that high molecular weight PLA can readily be obtained in the presence of transition metal compounds of tin, zinc, iron and aluminum, among others. A systematic investigation has led to the wide use of tin compounds, namely tin(II) bis-2-ethylhexanoic acid (stannous octoate) as a catalyst in PLA synthesis. This is mainly due to its high catalytic efficiency, low toxicity, food and drug contact approval and ability to give high molecular weights with low racemization. The mechanisms of the polymerization with stannous octoate have been studied in detail, and it is now widely accepted that this ROP is actually initiated from compounds containing hydroxyl groups, such as water and alcohols, which are either present in the lactide feed or can be added upon demand. Figure 65 shows that the global mechanism is of the ‘coordination–insertion’ type, occurring in two steps: first, a complex between monomer and initiator is formed followed by a rearrangement of the covalent bonds; then, the monomer is inserted within the oxygen–metal bond of the initiator, and its cyclic structure is thus opened through the cleavage of the acyl–oxygen link, thus the metal is incorporated with an alkoxide bond into the propagating chain. It was found that the polymerization yield and the transesterification effect are affected by different parameters, such as the polymerization temperature and time, the monomer/catalyst ratio and the type of catalyst. The interaction between the time and temperature is very significant in terms of limiting the degradation reactions, which affect the molecular weight and the reaction kinetics. It has also been shown that the chain length is directly controlled by the amount of OH impurities. To make an economically viable PLA, Jacobsen et al. developed a continuous one-stage process based on reactive extrusion with a twin-screw extruder. This technique requires that the bulk polymerization be close to completion within a very short time (5–7 min), which is predetermined by the residence time in the extruder.
These authors showed that the addition of an equimolar content of a Lewis base, particularly triphenyl-phosphine, to stannous octoate increased the lactide polymerization rate.

4.3 Properties

**Crystallinity and thermal properties**

The properties of PLA, as indeed those of other polymers, depend on its molecular characteristics, as well as on the presence of ordered structures, such as crystalline thickness, crystallinity, spherulite size, morphology and degree of chain orientation. The physical properties of polylactide are related to the enantiomeric purity of the lactic acid stereo-copolymers. Homo-PLA is a linear macromolecule with a molecular architecture that is determined by its stereo chemical composition. PLA can be produced in a totally amorphous or with up to 40 % crystalline. PLA resins containing more than 93% of L-lactic acid are semi-crystalline, but, when it contains 50–93% of it, it is entirely amorphous. Both meso- and D- lactides induce twists in the very regular PLLA architecture. Macromolecular imperfections are responsible for the decrease in both the rate and the extent of PLLA crystallization. In practice, most PLAs are made up of L- and D- lactide copolymers, since the reaction media often contain some meso-lactide impurities.

Depending on the preparation conditions, PLLA crystallizes in different forms. The α-form exhibits a well-defined diffraction pattern. This structure, with a melting temperature of 185°C, is more stable than its β-counterpart, which melts at 175°C. The latter form can be prepared at a high draw.
ratio and a high drawing temperature. The $\gamma$-form is formed by epitaxial crystallization. It has been observed that a blend with equivalent poly(L-lactide) PLA and poly(D-lactide) PDLA contents gives stereo-complexation (racemic crystallite) of both polymers. This stereo complex has higher mechanical properties than those of both PLAs, and a higher melting temperature of 230°C. The literature reports different density data for PLA, with most values for the crystalline polymer around 1.29 compared with 1.25 for the amorphous material. The crystallization kinetics of PLA have been extensively studied and found to be rather slow, as in the case of poly(ethylene terephthalate) PET.

The rate of crystallization increases with a decrease in the molecular weight and is strongly dependent on the (co)polymer composition. PLLA can crystallize in the presence of D-lactide, however, as the structure becomes more disordered, the rate of crystallization decreases. It has been reported that the crystallization rate is essentially determined by the decrease in the melting point of the different copolymers. PDLA/PLLA stereo complexes are very efficient nucleating agents for PLLA, with increases in both the crystallization rate and the crystallinity, the latter of up to 60%. Quenching decreases the crystallization time. As PET, PLA can be oriented by processing and chain orientation increases the mechanical strength of the polymer. If orientation is performed at low temperature, the resulting PLLA has a higher modulus without any significant increase in crystallinity. To determine the crystallinity levels by differential scanning calorimetry (DSC), the value most often referred to in the literature concerning the PLA melt enthalpy at 100% crystallinity, is 93 J g$^{-1}$. The crystallization of the thermally crystallizable, but amorphous PLA, can be initiated by annealing it at temperatures between 75°C and the melting point. Annealing crystallizable PLA copolymers often produces two melting peaks and different hypotheses have been put forward to explain this feature. Yasuniwa et al. found a double melting point in PLLA polymers and attributed them to slow rates of crystallization and recrystallization. The typical PLA glass transition temperature ($T_g$) ranges from 50°C to 80°C, whereas its melting temperature ranges from 130°C to 180°C. For instance, enantiomerically pure PLA is a semi-crystalline polymer with a $T_g$ of 55°C and a $T_m$ of 180°C. For semi-crystalline PLA, the $T_m$ is a function of the different processing parameters and the initial PLA structure. According to Ikada and Tsuji, $T_m$ increases with increasing molecular weight (Mw) to an asymptotic value, but the actual crystallinity decreases with increasing Mw. $T_m$, moreover, decreases with the presence of meso-lactide units in its structure. Both, the degree of crystallinity and the melting temperature of PLA-based materials can be reduced by random copolymerization with different comonomers (e.g. GA, CL or valerolactone).
The Tg of PLA is also determined by the proportion of the different types of lactide in its macromolecular chain.

**Surface energy**

Surface energy is critically important to many processes (printing, multilayering, etc.) and it influences the interfacial tension. The surface energy of a PLA made up of 92% L-lactide and 8% meson-lactide was found to be 49 mJ m\(^{-2}\), with dispersive and polar components of 37 and 11 mJ m\(^{-2}\), respectively, which suggests a relatively hydrophobic structure compared with that of other biopolysteres.

**Solubility**

A good solvent for PLA and for most of the corresponding copolymers is chloroform. Other solvents are chlorinated or fluorinated organic compounds, dioxane, dioxolane and furan. Poly(rac-lactide) and poly(meso-lactide) are soluble in many other organic solvents like acetone, pyridine, ethyl lactate, tetrahydrofuran, xylene, ethyl acetate, dimethyl formamide, methyl ethyl ketone. Among non-solvents, the most relative compounds are water, alcohols (e.g. methanol and ethanol) and alkanes (e.g. hexane and heptane).

**Barrier properties**

Because PLA finds a lot of applications in food packaging, its barrier properties (mainly to carbon dioxide, oxygen and water vapor) have been largely investigated. The CO\(_2\) permeability coefficients for PLA polymers are lower than those reported for crystalline polystyrene at 25°C and 0% relative humidity (RH) and higher than those for PET. Since diffusion takes place through the amorphous regions of a polymer, an increase in the extent of crystallization will inevitably result in a decrease in permeability. Figure 66 shows the oxygen permeability for poly(98% L-lactide) films as a function of the water activity. A significant increase in the oxygen permeability coefficient is shown as the temperature is increased, but, its decrease with water activity at temperatures close to Tg and its stabilization at temperatures well below Tg, are clearly visible. PET and PLA are both hydrophobic and the corresponding films absorb very low amounts of water, showing similar barrier properties, as indicated by the values of their water vapor permeability coefficient determined from 10°C to 37.8°C in the range of 40–90 % RH. Auras *et al.* have shown that the permeability for 98% L-lactide polymers is almost constant over the range studied, despite PLA being a rather polar polymer.
4.4 Mechanical properties

Solid state

The mechanical properties of PLA can vary to a large extent, ranging from soft and elastic materials to stiff and high strength materials, according to different parameters, such as crystallinity, polymer structure and molecular weight, material formulation (plasticizers, blend, composites, etc.) and processing (e.g. orientation). For instance, commercial PLA, such as poly (92% L-lactide, 8% meso-lactide), has a modulus of 2.1 GPa and an elongation at break of 9%. After plasticization, its Young’s modulus decreases to 0.7 MPa and the elongation at break rises of 200%, with a corresponding Tg shift from 58°C to 18°C. This example indicates that mechanical properties can be readily tuned to satisfy different applications.

Molten behavior

For processing and for the corresponding applications, the knowledge of PLA melt rheology is of particular interest. A power law equation has been applied successfully by, for example, Schwach and Averous. The pseudoplastic index is in the range 0.2–0.3, depending on the PLA structure. For
instance, poly(92% L-lactide, 8% meso-lactide) displays a pseudoplastic index of 0.23. Figure 67, based on data published by Dorgan et al., shows the evolution of the zero-shear viscosity versus molecular weight (Mw) for a wide range of L/D ratios (%), the latter parameter having virtually no effect. Static and dynamic characterizations have shown that the molecular weight between entanglements is around $10^4$. Some other studies suggested that chain branching and molecular weight distribution have a significant effect on the melt viscosity of PLA.

Figure 67. Zero-shear viscosity versus molecular weight for different L/D ratios (%)

\[
\log(\eta_0) = A + 3.4\log(M_w)
\]

<table>
<thead>
<tr>
<th>Value</th>
<th>s.e.e.</th>
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<tbody>
<tr>
<td>A</td>
<td>-14.26</td>
</tr>
<tr>
<td>R</td>
<td>0.987</td>
</tr>
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</table>
4.5 Degradation

Abiotic degradation
The main abiotic phenomena involve thermal and hydrolysis degradations during the life cycle of the material.

**Thermal degradation**
The thermal stability of biopolymesters is not significantly high, a fact that inevitably limits their range of applications. The PLA decomposition temperature is lies between 230°C and 260°C. Gupta and Deshmukh concluded that the carbonyl carbon–oxygen linkage is the most likely bond to split under isothermal heating, as suggested by the fact that a significantly larger amount of carboxylic acid end-groups were found compared with hydroxyl end-groups. The reactions involved in the thermal degradation of lactic acid-based polymers can follow different mechanisms, such as thermohydrolysis, zipper-like depolymerization in the presence of catalyst residues, thermo-oxidative degradation and transesterification reactions which give simultaneous bond breaking and bond making.

**Hydrolytic degradation**
PLA hydrolysis is an important phenomenon since it leads to chain fragmentation, and can be associated with thermal or biotic degradation. This process can be affected by various parameters such as the PLA structure, its molecular weight and distribution, its morphology (crystallinity), the shape of its samples and its thermal and mechanical history (including processing), as well as, of course, the hydrolysis conditions. Hydrolytic degradation is a phenomenon, which can be both desirable (e.g. during the composting stage) or undesirable (e.g. during processing or storage). The hydrolysis of aliphatic polyesters starts with a water uptake phase, followed by hydrolytic splitting of the ester bonds in a random way. The amorphous parts of the polyesters have been known to undergo hydrolysis before their crystalline regions because of a higher rate of water uptake. The initial stage is therefore located at the amorphous regions, giving the remaining non-degraded chains more space and mobility, which leads to their reorganization and hence an increased crystallinity. In the second stage, the hydrolytic degradation of the crystalline regions of the polyester leads to an increased rate of mass loss and finally to complete resorption. The PLA degradation in an aqueous medium has been reported by Li et al. to proceed more rapidly in the core of the sample. The explanation for this specific behavior is an autocatalytic effect due to the increasing amount of compounds containing carboxylic end-groups. These low molar mass
compounds are not able to permeate the outer shell. The degradation products in the surface layer are instead continuously dissolved in the surrounding buffer solution. As expected, temperature plays a significant role in accelerating this type of degradation.

**Biotic degradation**

The biodegradation of aliphatic biopolymesters has been widely reported in the literature. The biodegradation of lactic acid-based polymers for medical applications has been investigated in a number of studies *in vivo* and some reports can also be found on their degradation in other biological systems. The *in vivo* and *in vitro* degradations have been evaluated for PLA-based surgical implants. *In vitro* studies have shown that the pH of the solution plays a key role in the degradation and that this analysis can be a useful predicting tool for *in vivo* PLA degradation. Enzymes, such as proteinase K and pronate, have been used to bring about the *in vivo* PLA hydrolysis, although, enzymes are unable to diffuse through the crystalline parts. As expected, little enzymatic degradation occurs at the beginning of the process, but pores and fragmentation are produced, widening the accessible area to the different enzymes. Figure 68 shows that during the composting stage, PLA degrades in a multistep process with different mechanisms. Primarily, after exposure to moisture by abiotic mechanisms, PLA degrades by hydrolysis. First, random non-enzymatic chain-scissions of the ester groups lead to a reduction in molecular weight, with the consequent embrittlement of the polymer. This step can be accelerated by acids or bases and is affected by both temperature and moisture levels. Then, the ensuing PLA oligomers can diffuse out of the bulk polymer and be attacked by microorganisms. The biotic degradation of these residues produces carbon dioxide, water and humus (mineralization). Studies on PLA-based multiphase materials have been carried out. Gattin *et al.* have found that the physical and morphological properties of the blend play an important role in its degradation behavior, as in the case of their comparative study of the degradation of PLA with and without plasticized starch materials. These authors reported that the nature of the degradation strongly depends on the experimental biodegradation conditions. Sinha Ray *et al.* prepared PLA nano-biocomposites filled with montmorillonite and studied and characterized their biodegradability.
4.6 Processing

The extrusion of PLA-based materials is generally linked with another processing step such as thermoforming, injection molding, fiber drawing, film blowing, bottle blowing and extrusion coating. The properties of the polymer will therefore depend on the specific conditions during the processing steps (e.g. the thermo-mechanical input). The main parameters during the melt processing are temperature, residence time, moisture content and atmosphere. But, the major problem in the manufacturing of PLA-based products is the limited thermal stability during the melt processing. To overcome such a drawback or to give PLA new properties, a large number of multiphase materials have been developed, mainly by mixing PLA with others products.

Plasticization

The brittleness and stiffness of PLA can be major drawbacks for some application. According to Ljungberg et al., any factor influencing PLA crystallinity, such as the isomer ratio, could disturb the distribution and compatibility of plasticizers with PLA and induce low efficiency and phase separation. Lactide monomer is an effective plasticizer for PLA, but presents high migration due to its small molecular size. Oligomeric lactic acid (OLA) seems to be a better answer, since it shows
low migration and high efficiency. For instance, adding 20 wt% of OLA into poly(92 % L-lactide, 8% meso-lactide) induces Tg and modulus decreases of 20°C and 63%, respectively. A significant improvement of PLA (mainly PLLA) flexibility is accomplished by the incorporation of different types of citrates or maleates whose efficiency was evaluated in terms of Tg shift and mechanical properties improvement. These plasticizers are miscible with PLA up to ~25 wt%, but increasing the plasticizer content can raise the PLA crystallinity by enhancing chain mobility. Low molecular weight polyethylene glycol (PEG), polypropylene glycol and fatty acid are also compatible with PLA and can act as plasticizers.

**Blends and compatibilization**

A great number of articles has been published during the last few decades on PLA-based blends, including starch/PLA blends, which allow reducing the material cost without sacrificing its biodegradability and maintaining certain mechanical and thermal properties. Native starch, which is composed of semi-crystalline granules, can be physically blended with PLA, but remains in a separate conglomerate form in the PLA matrix. Thus, starch is typically characterized as a solid filler with poor adhesion with PLA. Such biocomposites are used as a model to test (e.g. carbohydrate–PLA compatibilization). Most of the studies which are focused on the production of starchy blends are based on plasticized starch, the so-called thermoplastic starch. Such a processable material is obtained by the disruption of the granular starch and the transformation of its semi-crystalline granules into a homogeneous, rather amorphous material with the destruction of hydrogen bonds between the macromolecules. Disruption can be accomplished by casting (e.g. with dry drums) or by applying thermo-mechanical energy in a continuous process. The combination of thermal and mechanical inputs can be obtained by extrusion. After the processing, a homogeneous material is obtained. A dependence of the PLA glass transition temperature on the blend composition was observed by DSC and DMA, indicating a small degree of compatibility between the blend components. However, the mechanical characteristics of the blends were modest. The blend morphology (discontinuous versus co-continuous) has been investigated by Schwach and Averous by microscopic observations. The full co-continuity is obtained in the domain of 60–80% in volume of PLA. Despite the interest in developing plasticized starch/PLA materials, some limitations, due to the lack of affinity between the respective constituents, seem difficult to overcome. This low compatibility is mainly due to the PLA hydrophobic character.

To improve the affinity between the phases, compatibilization strategies are generally developed. This implies the addition of a compound, the compatibilizer, which can be obtained by the
modification of at least one of the polymers initially present in the blend. For PLA/starch compatibilization, the literature proposes different approaches which can be classified in four groups: (i) the functionalization of PLA with, for example, maleic anhydride; (ii) the functionalization of starch with, for example, urethane functions; (iii) the starch–polyester crosslinking with a coupling agent such as a peroxide and (iv) the use of copolymers, for example, starch-graft PLA, following the mechanism discussed above, for which the length of the grafts can be controlled to obtain a comb structure.

It is known that PLA forms miscible blends with polymers such as PEG. PLA and PEG are miscible with each other when the PLA fraction is below 50%. The PLA/PEG blend consists of two semi-miscible crystalline phases dispersed in an amorphous PLA matrix. PHB/PLA blends are miscible over the whole range of composition. The elastic modulus, stress at yield, and stress at break decrease, whereas the elongation at break increases, with increasing poly(hydroxyl butyrate) (PHB) content. Both PLA/PGA and PLA/PCL blends give immiscible components, the latter being susceptible to compatibilization with P(LA-co-CL) copolymers or other coupling agents.

**Multilayer structures**

Developing compostable and low cost multilayer materials based for instance on plasticized starch and PLA is interesting in more than one sense. Martin *et al.* carried out several studies on such a system and showed that the basic requisites for the preparation of multilayered products are to obtain sufficient adhesion between the layers, good moisture barrier properties and a uniform layer thickness distribution. Two different techniques were used to prepare the multilayers, namely, coextrusion and compression molding. Peel strength was controlled by the compatibility between plasticized starch and PLA, which stayed low without compatibilizer. It was possible to increase the adhesion properties of the film by up to 50 % (*e.g.* by blending low polyester contents into the starchy core layer). There exist some inherent problems due to the multilayer flow conditions encountered in coextrusion, such as encapsulation and interfacial instability phenomena. Addressing these problems is a crucial issue, since they can be detrimental to the product, affecting its quality and functionality.
**Biocomposites and nano-biocomposites**

Different types of fillers have been tested with PLA, such as calcium phosphate or talc, which show an increase in its mechanical properties. Concerning inorganic fillers, the greatest reinforcing effect is obtained with whiskers of potassium titanate and aluminum borate with a high aspect ratio. Carbon or glass fibers improve the mechanical properties, particularly with fiber surface treatments capable of inducing strong interactions with PLA matrix. Different organic fillers can be associated with PLA. Biocomposites with improved mechanical properties are obtained by the association of ligno-cellulose fillers, such as paper-waste fibers and wood flour, with PLA by extrusion and compression molding.

A significant and increasing number of papers have been published during the last 5 years on nano-biocomposites (i.e. nanocomposites based on a biodegradable matrix). Polylactide_layered silicate nanocomposites were largely investigated by Sinha Ray et al. and other authors. They successfully prepared a series of biodegradable PLA nano-biocomposites using mainly melt extrusion of PLA, principally with modified montmorillonites (O-MMT), targeting nanofillers exfoliation into the matrix. Because of the interactions between the organo-clay particles which present large surface area and the PLA matrix, the nano-biocomposites displayed improved properties, such as mechanical moduli, thermal stability, crystallization behavior, gas barrier and biodegradability. The preparation of biodegradable nanocellular polymeric foams via nanocomposites technology based on PLA and layered silicate has been reported by different authors who used supercritical carbon dioxide as a foaming agent, with the silicate acting as nucleating site for cell formation. Cellular PLA structures can also be obtained by producing a co-continuous structure and extracting the co-products.

**4.7 Applications**

At present, PLA-based materials are mainly referenced on three different markets, namely, the biomedical (initial market), the textile (mainly in Japan) and the packaging (mainly food, i.e. short-term applications). For instance, reported types of manufactured products are blow-molded bottles, injection-molded cups, spoons and forks, thermoformed cups and trays, paper coatings, fibers for textile industry or sutures, films and various molded articles.
PLA has been widely studied for use in medical applications because of its bioresorbability and biocompatible properties in the human body. The main reported examples on medical or biomedical products are fracture fixation devices like screws, sutures, delivery systems and micro-titration plates. PLA-based materials are developed for the production of screws and plates. As the bone healing progresses, it is desirable that the bone is subjected to a gradual increase in stress, thus reducing the stress-shielding effect. This is possible only if the plate loses rigidity in \textit{in vivo} environment. To meet this need, researchers introduced resorbable polymers for bone plate applications. PLA resorbs or degrades upon implantation into the body, but most of its mechanical properties are lost within a few weeks. Tormala \textit{et al.} proposed fully resorbable composites by reinforcing matrices with resorbable PLLA fibers and calcium phosphate-based glass fibers. One of the advantages often quoted for resorbable composite prostheses is that they do not need to be removed with a second operative procedure, as with metallic or non-resorbable composite implants. To improve the mechanical properties, PLA is reinforced with variety of non-resorbable materials, including carbon and polyamide fibers. Carbon fibers/PLA composites possess very high mechanical properties before their implantation, but they lose them too rapidly \textit{in vivo} because of delamination. The long-term effects of resorbed products, and biostable or slowly eroding fibers in the living tissues are not fully known, and are concerns yet to be resolved. Although PLA fibers are used in different textile applications as, for example, non-woven textile for clothes, they achieved their first commercial success as resorbable sutures. One of the first commercially available fiber formed bioresorbable medical products is based on copolymers of GA in combination with L-lactide (Vicryl).

Fibers can be produced both by solvent and by melt-spinning processes and drawn under different conditions to orient the macromolecules.

Micro- and nano- particles are an important category of delivery systems used in medicine, and the use of PLA is interesting due to its hydrolytic degradability and low toxicity. The most important properties of the micro- and nano- particles are the drug release rate and the matrix degradation rate which are affected by the particle design and the material properties. Copolymers of GA and rac-lactide seem to be the most suitable combinations for use as drug delivery matrices.

Porous PLA scaffolds have been found to be potential reconstruction matrices for damaged tissues and organs. There are several techniques reported for the manufacturing of such materials.

\textit{Packaging applications}
Commercially available PLA packaging can provide better mechanical properties than polystyrene and have properties more or less comparable to those of PET. Market studies show that PLA is an economically feasible material for packaging. With its current consumption, it is at the present the most important market in volume for biodegradable packaging. Due to its high cost, the initial use of PLA as a packaging material has been in high value films, rigid thermoforms, food and beverage containers and coated papers. One of the first companies to use PLA as a packaging material was Danone (France) in yoghurt cups for the German market. During the last decade, the use of PLA as a packaging material has increased all across Europe, Japan and the US, mainly in the area of fresh products, where PLA is being used as a food packaging for short shelf-life products, such as fruit and vegetables.

Package applications include containers, drinking cups, sundae and salad cups, wrappings for sweets, lamination films, blister packages and water bottles. Currently, PLA is used in compostable yard bags to promote national or regional composting programs. In addition, new applications such as cardboard or paper coatings are being pursued, for example, the fast-food market (cups, plates and the like). However, to cater for a larger market, some PLA drawbacks must be overcome, such as its limited mechanical and barrier properties and heat resistance, and, in order to meet market expectations, the world production of PLA must be substantially increased.
5. POLYVINYL CHLORIDE

5.1 Introduction

PVC is a derivative of ethylene and is referred to as a vinyl polymer. It is an addition polymer with vinyl chloride as monomer (VCM) and is characterized by the \(~[\text{CH}_2\text{CHCl}]_n~\) repeating unit (Figure 69).

![Figure 69. Vinyl chloride polymerization](image)

PVC was first prepared by the German chemist Eugen Baumann in 1872, but it was not patented until 1913, when Friedrich Heinrich August Klatte used sunlight to initiate the polymerization of vinyl chloride. Commercial application of this plastic was limited by its extreme rigidity. In 1926, while trying to dehydrohalogenate PVC in a high-boiling solvent in order to obtain an unsaturated polymer that might bond rubber to metal, Waldo Lonsbury Semon, working for the B.F. Goodrich Company in the United States, obtained what is now called plasticized PVC. The discovery of this flexible, inert product was responsible for the commercial success of the polymer. Another route to a flexible product was copolymerization: in 1930 the Union Carbide Corporation introduced the trademarked polymer Vinylite, a copolymer of vinyl chloride and vinyl acetate that became the standard material of long-playing phonograph records.

Today PVC, with 37.4 million t in 2012 is in third place behind polyolefins in terms of global plastic consumption. Average annual market growth of 4.9% in the period from 2009 to 2012 occurred largely in China, the largest single market, with 14 million t (Figure 70). Regarding worldwide production capacity, in 2012 was 54 million t (source IHS); an increase of 9 million t since 2009, when the world demand for PVC decreased significantly due to the global economic crisis. However, the construction market is still in crisis in Europe and North America, it can be stated that it is mainly driven by CIS, Asia Pacific and Latin American countries, such as Russia, China, Brazil, etc. Most of the capacity increase is occurring in China, which now has about 44% of the world’s capacity. Global PVC market is strongly connected to construction industry; main end-uses in 2012 were pipes and fittings, profiles and hose/tubing, rigid film and sheets. Other
applications include cables, flooring, coatings, etc. (Figure 71). Figure 72 shows the production capacities of the world’s largest producers.

Figure 70. Worldwide PVC consumption in 2012, broken down by region (overall 37,400 kt) (Source: IHS/Vinnolit)

Figure 71. PVC applications around the world in 2012 (Source: IHS)
What makes PVC unique can be considered under three headings: morphology, versatility and molecular structure. Regarding morphology the as made PVC, is particulate in nature and comes in two main sizes depending on the process used. Suspension and mass polymerizations give grains (particles) of 100 – 180mm in diameter, whereas the emulsion process affords a latex of particle size 0.1 – 3.0mm. Poly(vinyl chloride) is a generic name. Each producer makes a range of PVC polymers which vary in morphology and in molecular mass, depending on the intended end use. K-value and viscosity number are used to represent molecular mass, and producers often reflect these parameters in the grade codes used to define different products (e.g., S 68/173 refers to a suspension type material with a K-value of 68, and VY 110/57 to a resin with a viscosity number of 110). PVC
with $K = 66 - 68$ can be processed in rigid formulations to give pipes, conduit, sheet, and window profiles; $K = 65 - 71$ in flexible formulations for flexible sheet, flooring, wallpapers, cable coverings, hoses, tubing, and medical products, and PVC with low $K$-values ($55 - 60$) in formulations for injection molding of pipe and conduit fittings, integral electrical plugs, and blow molding of bottles and other containers.

Considering the molecular structure, amongst the range of polymeric materials produced today PVC is unique because the bulky chlorine atom imparts a strongly polar nature to the PVC polymer chain, and the essentially syndiotactic conformation of the repeat unit in the chain leads to a limited level of crystallinity, maximum 5%. This results in good mechanical properties, particularly stiffness at low wall thickness, high melt viscosity at relatively low molecular mass, and the ability to maintain good mechanical properties even when highly plasticized. This enables a wide range of softness and flexibility to be achieved and hence leads to an even wider variety of end uses. Moreover PVC is never used alone, it is always mixed with heat stabilizers, lubricants, plasticizers, fillers, and other additives to make processing possible, all of which can influence its physical and mechanical properties.

### 5.2 Production of PVC

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

In suspension polymerization liquid vinyl chloride is dispersed in water by mechanical stirring. The fine droplets of VCM remain in suspension as long as the agitation continues. Polymerization is carried out in pressurized vessel under the influence of heat and initiators and/or catalysts, which are soluble in the monomer. A typical initiator is organic peroxide. The reaction is exothermic and the heat evolved is removed in order to keep reaction temperature constant. Suspension agents known as protective colloids are added to the reactor to prevent the monomer droplets coalescing and the polymer particles from agglomerating. When the desired conversion is reached, the batch is transferred to a blow down vessel. Several batches may be transferred to this vessel for blending. Unreacted monomer is extracted from the polymer, recovered and recycled back to the polymerization reactor. Then the polymer particles are dried.

By choosing suitable stabilizers and plasticizers, suspension polymerized PVC (S-PVC) can be converted into a wide variety of different products. S-PVC is used for most rigid PVC applications such as pipes, profiles, other building materials and hard foils. It can also be plasticized and used
for most flexible applications such as cable insulation, soft foils and medical products. Building and construction is the predominant market of S-PVC. Figure 73 reports the example of a plant for suspension polymerization.

![Figure 73. Suspension PVC plant: a) Reactor; b) Blowdown vessel; c) VCM recovery plant; d) Stripping column; e) Heat exchanger; f) Centrifuge; g) Driers](image)

The emulsion polymerization can be conducted by: batch emulsion, continuous emulsion, or micro-suspension (Fig.6). All three routes produce an aqueous latex, i.e. a very fine suspension of PVC polymer with mean particle sizes between 0.1 and 3 μm and thus much smaller than those produced by suspension polymerization. Liquid vinyl chloride is insoluble in water and disperses to fine droplets when mechanically agitated in presence of an emulsifier. The reaction takes place in pressurized vessels under the influence of heat, initiators and/or catalysts. In the batch process, the polymerization takes place at the VCM–water interface with a water-soluble initiator. In the continuous process, VCM, emulsifiers and initiator are fed into the reactor and PVC latex is withdrawn continuously. Alternatively, micro-suspension produces latex with a wider particle size distribution: here, polymerization takes place within the dispersed VCM droplets, with an initiator highly soluble in VCM, but not in water. In each case, the reaction is exothermic and heat is removed in order to keep temperatures constant. Latex is transferred to a blow-down vessel; unreacted monomer is extracted, recovered and recycled back to the polymerization reactor. The polymer particles are then dried.
By choosing suitable stabilizers and plasticizers, emulsion PVC (E-PVC) can be converted into a wide variety of different products. E-PVC can be extruded in rigid profiles when high surface gloss and smoothness are required. But mainly, E-PVC is dispersed in plasticizer to produce a mix known as plastisol. Plastisol is spread or sprayed, then heat-cured. Typical applications are cushion flooring, wall coverings, coated fabrics, gloves, rotational and slush moldings, such as interior car parts, steel coatings and automotive under-body sealants.

Mass (bulk) polymerized PVC is used extensively in rigid extrusion applications on a worldwide scale. The process is carried out in two stages. In the first stage the monomer and the initiator are charged and vigorously stirred in a prepolymerizer autoclave, then in the second stage the slurry from the prepolymerizer is discharged into the second stage reactor with fresh initiator and more VCM. As the conversion increases the physical nature changes from a wet to a dry powder. The final grain of PVC in this case are 130-160 μm in diameter.

![Figure 74. Schematic representation of the stages required for a plant which produces all emulsion, seeded, and microsuspension grades](image-url)

### 5.3 Flexible PVC
The largest volume PVC resin type used in flexible and semi-rigid applications is aqueous suspension PVC homopolymer, made to have sufficient porosity in the particles to absorb enough plasticizer to meet the desired flexibility and hardness specifications of the intended end-product. For most flexible uses, the resins range from medium to high molecular weight. By normally accepted conventions this means from approx. 30,000 to approx. 60,000 number average molecular weight. In terms of commonly used tests based on dilute solution viscosity, this means from approx. 0.57 to 1.10 inherent viscosity, or from approx. 51 to 71 Fikentscher K. Flexible PVC products injection-molded or extruded at very high shear rates may be made with low molecular weight PVCs having less than 30,000 number average molecular weight. However, using PVC resins with such low molecular weights sacrifices physical properties, including compression set, elongation at failure, tensile strength, tear strength, and fatigue resistance. It is difficult to make ultra-low molecular weight PVC resins having high particle porosities. Very low molecular weight resins are not used for highly flexible items, because items made with them are too weak. When formulating flexible PVC compounds for specific exacting uses, many compromises are often involved in selecting the best resin. For instance, other things being equal, the higher the molecular weight of the chosen resin, the higher the processing temperature needs to be during fabrication in order to achieve optimal fusion. Also, for a given processing temperature, use of higher molecular weight PVCs tends to give lower gloss on a finished product. If low gloss is required on an extruded product, which otherwise calls for use of a medium molecular weight PVC, it is necessary to specify a specialty “low gloss” resin offered by a few PVC manufacturers.

The particle shapes, size limits, size distribution, and internal porosities of the PVC grains formed during suspension or mass polymerization processes are very important parameters for flexible applications since particle sphericity tends to provide good bulk flow behavior along with efficient particle packing and higher bulk density in dry blends, while irregular, knobby resin particles, broad particle size distributions, and high particle porosity tend to give low bulk density and poor bulk flow behavior. For flexible applications, a relatively narrow PVC particle size distribution is desirable and is mandated by many users’ specifications. The aim point for average particle size (APS) is normally between 100 and 80 mesh. That is between 149 and 177 microns. For special purposes, suspension and mass. PVC resins may have their APSs skewed to finer or coarser numbers.

5.4 Additives
Before PVC can be made into products, it has to be combined with a range of special additives. The essential additives for all PVC materials are stabilizers and lubricants; in the case of flexible PVC, plasticizers are also incorporated. Other additives which may be used include fillers, processing aids, impact modifiers and pigments. Additives will influence or determine the mechanical properties, light and thermal stability, color, clarity and electrical properties of the product. Once the additives have been selected, they are mixed with the polymer for the compounding. One of the method for compounding uses an intensive high-speed mixer that intimately blends all the ingredients. The result is a powder, known as a ‘dry blend’, which is then fed into the processing equipment. The second compounding method consist in blending the ingredients in either a low or high-speed mixer and then transfer the powder to a melt compounder. This can either be a compounding extruder, or other special equipment for making PVC compounds. These produce a melt which, when cool, is cut into granules ready for processing. In a specialized process, liquid compounds known as plastisols, are produced as dispersions of very fine PVC polymer particles in liquid organic media. PVC compounds are made into products using a variety of processing methods which include extrusion, injection molding, blow molding, calendering, spreading and coating.

**Plasticizers**

A wide range of plasticizers are used in formulations, but the most widely used are C4–C12 esters such as phthalates, adipates, azelates, sebacates, trimellitates, and phosphates. Chlorinated paraffins are used as secondary plasticizers. A good plasticizer should have low volatility, low color value, neutral reaction, resistance to hydrolysis, insolubility in water, flame resistance, and non toxicity. As no plasticizer can satisfy all these properties several plasticizers are mixed to achieve the desired properties of the final product. Moreover, the amount of plasticizer used in formulations plays a major role in determining the hardness and flexibility of the end product and can vary from 40 to 130 phr.

**Heat stabilizers**

Metal compounds are usually employed as heat stabilizer. The major metals contained in stabilizers are lead (Pb), barium (Ba), calcium (Ca), and tin (Sn). The stabilizers are classified into Pb stabilizers, Ba-Zn stabilizers, CA-Zn stabilizers, and Son stabilizers. Ba-Zn stabilizers and Ca-Zn stabilizers are used as metallic soaps such as stearates, while Sn stabilizers are used as organic tin (dialkyl tin compounds). Other than metallic soap, Pb stabilizers are used as basic sulphate, basic
carbonate, or basic phosphate. Metal free stabilizer are also employed: phosphites, epoxy compounds, polyols and layered double hydroxide.

**Dyes and pigments**
The most widely used is titanium dioxide.

**Fillers**
Generally inorganic materials such as calcium carbonate, barite, silicate, kaolin or china clay, are used as filler primarily to lower costs and also to impart special properties such as hardness, abrasion resistance, and no sticking.

**Blowing agents**
For foamed PVC production compounds such as azo dicarbonamide are used.

**UV absorbers**
UV absorbers are used to prevent the decomposition action of sunlight.

**Antistatic agents**
Esters of poly(ethylene glycol), phosphate esters, and fatty acid amines and amides are usually employed.

**Viscosity depressants**
Poly(ethylene glycol) monolaurate, alkylphenols, low molecular mass paraffins are used to lower viscosity.

**Extender resin or filler polymer**
A PVC grade of spherical form, made by the suspension process and therefore cheaper than dispersion resin, can be added to reduce cost and viscosity.

**5.4.1 Plasticizers**
Several theories have been developed to account for the observed characteristics of the plasticization process.

According to the Free volume theory when molecules such as plasticizer are added to the polymer the Tg (glass transition temperature) of the polymer lowers, since plasticizer act separating the polymer macromolecules, adding free volume and making therefore the polymer soft and rubbery, but the plasticizer must be selective in interring the amorphous PVC part and must not enter and destroy the crystalline part of PVC, that acts as physical crosslink.

For a plasticizer to be effective and useful in PVC, it must contain two types of structural components, polar and apolar. The polar portion of the molecule must be able to bind reversibly
with the PVC polymer, thus softening the PVC, while the non-polar portion of the molecule allows the PVC interaction to be controlled so it is not so powerful a solvator as to destroy the PVC crystallinity. It also adds free volume, contributes shielding effects, and provides lubricity. Examples of polar components would be the carbonyl group of carboxylic ester functionality or, to a lesser extent, an aromatic ring; the non-polar portion could be the aliphatic side chain of an ester. The balance between the polar and non-polar portions of the molecule is critical to control its solubilizing effect; if a plasticizer is too polar, it can destroy PVC crystallites; if it is too non-polar, compatibility problems can arise.

### Table 9. Typical Properties of General Purpose Vinyl Plastic Products (phr: part per hundred resin, by weight)

<table>
<thead>
<tr>
<th></th>
<th>Rigid</th>
<th>Semirigid</th>
<th>Flexible</th>
<th>Very flexible</th>
<th>Extremely Flexible</th>
</tr>
</thead>
<tbody>
<tr>
<td>DINP, phr</td>
<td>0</td>
<td>34</td>
<td>50</td>
<td>80</td>
<td>600</td>
</tr>
<tr>
<td>Wt. % of composition</td>
<td>0</td>
<td>25</td>
<td>33</td>
<td>44</td>
<td>86</td>
</tr>
<tr>
<td><strong>Typical properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity, 20/20 °C</td>
<td>1.40</td>
<td>1.26</td>
<td>1.22</td>
<td>1.17</td>
<td>1.02</td>
</tr>
<tr>
<td>Hardness Durometer A,15s</td>
<td>-</td>
<td>94</td>
<td>84</td>
<td>66</td>
<td>&lt;10</td>
</tr>
<tr>
<td><strong>Flexural stiffness</strong> at 23 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPA</td>
<td>&gt;900</td>
<td>69</td>
<td>12</td>
<td>3.4</td>
<td>-</td>
</tr>
<tr>
<td>Psi</td>
<td>&gt;130,000</td>
<td>10,000</td>
<td>1700</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td><strong>Tensile strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPA</td>
<td>&gt;41</td>
<td>31</td>
<td>21</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Psi</td>
<td>&gt;6000</td>
<td>4,500</td>
<td>3,100</td>
<td>2,000</td>
<td>-</td>
</tr>
<tr>
<td>Elongation (%)b</td>
<td>&lt;15</td>
<td>225</td>
<td>295</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td><strong>Brittleness</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td>&gt;23</td>
<td>-16</td>
<td>-32</td>
<td>-47</td>
<td>-</td>
</tr>
<tr>
<td>°F</td>
<td>&gt;73</td>
<td>+3</td>
<td>-26</td>
<td>-53</td>
<td>-</td>
</tr>
<tr>
<td><strong>Examples</strong></td>
<td>Bottles, pipe, siding, records</td>
<td>Shades, shoe heels, thin films, produce wrap</td>
<td>Wall-covering, book-binders, upholstery, garden hose</td>
<td>Boots, gloves, water beds</td>
<td>Fishing lures</td>
</tr>
</tbody>
</table>

a ASTM D 747
b ASTM D 882
c ASTM D 746

d All plasticizer can be divided into three categories, related to their characteristic performance in PVC: general purpose plasticizer, performance stabilizer and specialty stabilizer. They are phthalates, trimellitates, aliphatic dibasic esters, polyesters, epoxides, phosphates and miscellaneous. Phthalates are the most widely used class of plasticizers in PVC. They contribute the most complete array of required performance properties in flexible PVC. In addition, their cost and
availability supports their preference. While historically DOP –di(2-ethylhexyl) – phthalate has been the product of choice, the current market for general purpose plasticizers includes dialkyl phthalates that are slightly different homologues of DOP, such as diisoheptyl (C7), diisooctyl (C8), diisononyl (C9) and diisodecyl (C10) phthalates; their combined usage totals more than 80% of the worldwide plasticizer market.

In table 9 are summarized the influence of a typical general purpose plasticizer DINP (di(isononyl) on PVC properties. As can be seen, the amount of plasticizer is also strongly influencing the properties.

### 5.5 Properties

PVC has unique features in terms of performance and functions as compared with olefin plastics which have only carbon and hydrogen atoms in their molecular structures. The properties of rigid PVC, containing a total additives amount of <10 % by weight are listed in table 10.

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

Regarding flexible PVC, the range of physical properties varies widely, depending on the plasticizer content. The main properties that are often specified are listed below.
Tensile strength and elongation at failure (ASTM D638) depend primarily on the level and type of plasticizer or other flexibilizer in the formulation, but also on resin molecular weight. Higher molecular weight resins in fully fused formulations give higher tensile strength and elongation at failure. 100% Modulus, defined as tensile stress at 100% elongation, is a useful measure of the stiffness of plasticized PVC, because it is relatively easy to measure accurately and reproducibly. For historical reasons, DOP is generally recognized as the bench mark plasticizer for PVC. With a medium-high molecular weight PVC, at 23 °C, DOP at 25 phr (part per hundred resin, by wt.%) gives a 100% modulus of about 22.8 MPa (3300 psi), which is classified as semi-rigid. Between 35 phr DOP and approx. 85 phr DOP (100% modulus 4.48 MPa or 650 psi), PVC is considered flexible. Above 85 phr DOP, PVC is called highly flexible. When comparing the efficiencies of different plasticizers, substitution factors (SFs) compared to DOP are generally used. However, most authors calculate these from Shore hardness measurements, which do not correlate exactly with 100% modulus. Figure 75 shows the comparison of tensile strength of PVC products with other plastics.

The brittleness temperature of flexible PVC is generally measured by ASTM D-746, which is a cold impact test run on specimens punched from standard test sheets 1.9±0.25 mm thick. However, on calendered PVC films, some people prefer to use the Masl and Impact Test (ASTM D1790). This test is run on films 0.25 mm or less in thickness under specified impact conditions. In this test,
the results are sensitive to the direction of sampling and the direction of fold due to the molecular orientation effects of calendering. In commercial laboratories the low temperature properties of flexible PVC are often estimated from stiffness measurements run by ASTM D 1043, which measures apparent modulus of rigidity, $G$, at different temperatures. The way D1043 is run, the angular deflection may extend beyond the elastic limits of the plastic at lower temperatures, so that the result is “apparent” rather than an actual modulus of elasticity, $E$, as measured by ASTM D 747. To convert $G$ to $E$, the simplifying assumption is made that $E = 3G$, which is only true if Poisson’s Ratio for the material under test conditions is 0.5. The temperature at which $E = 931$ MPa is reported as $T_f$, the flex temperature, which is the temperature at which the material is considered to have lost most of its elastomeric properties. Sometimes $T_4$, ($E = 6.90$ MPa) regarded as the upper end of a material’s useful temperature range, is also reported. Academic laboratories generally use more precise methods of measuring moduli as function of temperature.

**Abrasion resistance** of flexible PVC is often measured by the Taber Abrasion Test (ASTM D 4060). Results are reported as weight loss per 1000 cycles under conditions agreed to between the interested parties. Results are important for automobile undercoatings, boot and shoe soles, floor coverings, mine belts, and electrical cords for use under harsh conditions.

**The hardness** of flexible PVC materials is commonly measured by Shore Hardness (ASTM D 2240) using the A scale. Sometimes the D scale is used on semi-rigid compounds with plasticizer levels at or below 40 phr DOP equivalent. Conditioning of test specimens at the test temperature is critical.

**The heat distortion temperature** is the temperature when the test piece placed in the heat medium with bending load applied reaches a specified deflection as temperature rises. The Vicat softening temperature is defined as the temperature where the needle shaped penetrator sinks into the test piece to a specified depth as temperature of the heating medium rises and specified vertical load is applied to the test piece.

Table 11 and 12 show the thermal deformation temperature and the softening temperature (called “Vicat softening temperature”) of major plastics.
Plastics & Heat Distortion Temperature (°C)

<table>
<thead>
<tr>
<th></th>
<th>Heat Distortion Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>54 ~ 80</td>
</tr>
<tr>
<td>PS (general purpose)</td>
<td>&lt; 104</td>
</tr>
<tr>
<td>PS (impact resistant)</td>
<td>&lt; 99</td>
</tr>
<tr>
<td>ABS</td>
<td>104 ~ 106</td>
</tr>
<tr>
<td>HDPE</td>
<td>43 ~ 49</td>
</tr>
<tr>
<td>LDPE</td>
<td>32 ~ 41</td>
</tr>
<tr>
<td>PP</td>
<td>57 ~ 64</td>
</tr>
<tr>
<td>PC</td>
<td>130 ~ 138</td>
</tr>
</tbody>
</table>

Source “Practical dictionary of plastic terminology” edited by the Osaka Municipal Technical Research Institute

Table 12. Vicat softening point of PVC and other plastics

<table>
<thead>
<tr>
<th></th>
<th>Vicat Softening Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>102.5</td>
</tr>
<tr>
<td>ABS</td>
<td>102.3</td>
</tr>
<tr>
<td>PVC</td>
<td>92.0</td>
</tr>
<tr>
<td>PC</td>
<td>156.2</td>
</tr>
<tr>
<td>PE</td>
<td>127.3</td>
</tr>
<tr>
<td>PP</td>
<td>152.2</td>
</tr>
</tbody>
</table>

Source “Practical dictionary of plastic terminology” edited by the Osaka Municipal Technical Research Institute

**Aging after processing** is also very important. This is explained as being due to the slowness with which PVC crystallites reform after processing. For accurate results, at least one week of aging at 23 °C (73 °F) is recommended. Hardness readings increase with age after molding or other processing. Note also that Shore hardness readings drop rapidly during the first several seconds after specimen contact. For vinyl plastics, ASTM specifies taking Shore A hardness readings after 15 seconds. However, many commercial laboratories use 10 second Shore hardness. Test sample thickness is critical. ASTM specifies using specimens molded to 0.64 cm thickness. On calendered or extruded films and sheets, many laboratories stack several thicknesses, but this is less precise than using specimens molded to 0.64 cm thickness. In commercial quality control testing, operators never wait until Shore hardness has stabilized before testing. They specify definite aging and conditioning periods of usually less than a day. In the United Kingdom, British Standard Softness (B.S. 2782:32A) is generally specified. This test correlates well with 15 s Shore A hardness in the
sense that a plot of Shore A hardness against British Standard softness is a straight line. The same considerations regarding aging and conditioning of flexible PVC specimens apply as for Shore Hardness testing. For flexible PVC compounds used as primary insulation on electrical wires and for electrical tapes, electrical properties are critical. Tests commonly used include dielectric constant (ASTM D150), dielectric strength (ASTM D149), and volume and surface resistivity (ASTM D 257). The Underwriters’ Laboratories Insulation Resistance Test is specified for insulation compounds to be used on wires slated for use in wet locations.

The fire resistance of most flexible PVCs is less than that of rigid PVC. However, formulations can be devised to meet stringent flammability requirements, such as those for plenum cables. These require enough flexibility for installation in confined spaces and must also pass the UL-910 (NFPA 262) test. Other flammability tests often used on flexible PVC products include: the UL-VW-1 Vertical Wire Flame Test; the Oxygen Index Test (ASTM D2863); the DOT 302 MVSS Test for materials used in automobile interiors; the UL-94 Test run in the horizontal or vertical modes; the UL Vertical Tray Flame Test (UL 1581 for tray cables); and the UL-1666 Test for riser cables. The Cone Calorimeter Test, ASTM E1354, can be used to rank small samples of flexible vinyl materials for rate of heat release after ignition, ease of ignition, and emission of obscurational smoke. The test is versatile, because the heat flux to which samples are exposed can be varied from about 10 to 100 kW/m². Rate of heat release, sample mass loss rate, and smoke are measured or calculated from measured parameters. For smoke evolution, the NBS Smoke Chamber Test (ASTM E662) is still used, because many laboratories have the equipment. Cone calorimeter results are acknowledged to be more meaningful.

In any case PVC has inherently superior fire retarding properties due to its chlorine content, even in the absence of fire retardants. For example, the ignition temperature of PVC is as high as 455°C, and is a material with less risk for fire incidents since it is not ignited easily. Furthermore, the heat released in burning is considerably lower with PVC, when compared with those for PE and PP. PVC therefore contributes much less to spreading fire to nearby materials even while burning. Because Burning PVC yields an expanded carbonaceous structure usually called ‘intumescence’. This structure forms a thermal barrier protecting underlying parts.
Figure 76. Flash ignition and ignition temperatures of materials. Source: “PVC and Polymer” Vol. 29 (1989)

Table 13. Maximum heat release by various materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum heat release (kW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>91</td>
</tr>
<tr>
<td>Fire resistant ABS</td>
<td>250</td>
</tr>
<tr>
<td>Fire resistant PS</td>
<td>315</td>
</tr>
<tr>
<td>ABS</td>
<td>746</td>
</tr>
<tr>
<td>PS</td>
<td>859</td>
</tr>
<tr>
<td>Polyester</td>
<td>1216</td>
</tr>
<tr>
<td>PE</td>
<td>1325</td>
</tr>
<tr>
<td>PP</td>
<td>1335</td>
</tr>
</tbody>
</table>

Table 14. Oxygen Index values for PVC and several polymeric materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Oxygen Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytetrafluoroethylene</td>
<td>95.0</td>
</tr>
<tr>
<td>PVC</td>
<td>45 ~ 49</td>
</tr>
<tr>
<td>PC</td>
<td>26 ~ 28</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>24 ~ 29</td>
</tr>
<tr>
<td>PET</td>
<td>20.0</td>
</tr>
<tr>
<td>PS</td>
<td>17.6 ~ 18.3</td>
</tr>
<tr>
<td>PP</td>
<td>17.4</td>
</tr>
<tr>
<td>PE</td>
<td>17.4</td>
</tr>
</tbody>
</table>


There may be many ways of evaluating the fire retarding properties, but the oxygen index can be used for the evaluation with a comparatively high precision and reproducibility of the results. It represents the minimum oxygen concentration required for the test piece to continue burning in a mixed gas of oxygen and nitrogen. When the value is higher, the fire retarding property is higher. Since the oxygen concentration in the air is 21%, a plastic with an oxygen index greater than 22 has self-extinguishing property, while a plastic with oxygen index smaller than 21 is flammable (Table 14).

**Durability** under normal conditions of use is a key property. The factor most strongly influencing the durability of a material is resistance to oxidation by atmospheric oxygen. PVC, having the molecular structure where the chlorine atom is bound to every other carbon chain, is highly resistant to oxidative reactions, and maintains its performance for a long time. Other general purpose plastics with structures made up only of carbon and hydrogen are more susceptible to deterioration by oxidation in extended use conditions (such as, for example, through repeated recycling). Measurements on underground 35 year-old PVC pipes taken by the Japan PVC Pipe & Fittings Association showed no deterioration and the same strength as new pipes.
Research in Germany (60 Jahre Erfahrungen mit Rohrleitungen aus Weichmachfreiem PVC, 1995, KRV) has shown that soil buried pipes dug up after 60 years of active use when analyzed were proven to be fit for purpose and likely to have a further life expectancy of 50 years. Almost no deterioration was observed upon recovery of three kinds of automobile exterior accessories (flexible PVC products using plasticizers) from end-of-life cars after 13 years of use and upon comparison of physical properties with new products.

The shortened time for thermal decomposition is due to the heat history in the re-converting process, and can be brought back to that of the original products by adding stabilizers. Recovered products can in fact be recycled into the same products through re-converting, regardless of whether they are pipes or automobile parts. The physical properties of these re-converted products are almost the same as with products made from virgin resin, and there is also no problem upon actual use.

**The Oil/Chemical resistance** of PVC is very good. PVC is resistant to acid, alkali and almost all inorganic chemicals (Table 15). Although PVC swells or dissolves in aromatic hydrocarbons, ketones, and cyclic ethers, PVC is hard to dissolve in other organic solvents. Taking advantage of this characteristic, PVC is used in exhaust gas ducts, sheets used in construction, bottles, tubes and hoses.

---

**Table 15. Chemical resistance of PVC and other plastics**
<table>
<thead>
<tr>
<th>Plastics</th>
<th>Organic solvents</th>
<th>Salts</th>
<th>Alkalis</th>
<th>Acids</th>
<th>Oxidizing Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 66</td>
<td>7</td>
<td>10</td>
<td>7</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>PC</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Polyester (Chemical resistant)</td>
<td>6</td>
<td>10</td>
<td>4</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>PE</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Polyfluorocarbon</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>4</td>
<td>10</td>
<td>7</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>PP</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>PS</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>PU</td>
<td>8</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>PVC (flexible)</td>
<td>4</td>
<td>10</td>
<td>9</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>PVC (rigid)</td>
<td>6</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>ABS</td>
<td>4</td>
<td>10</td>
<td>8</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>6</td>
<td>10</td>
<td>7</td>
<td>9</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: the 1-10 scale has been set by empirical means. Higher value shows higher effectiveness.
Source: “Plastic almanac” by Kyogyo Chosakai Publishing Co. Ltd.

**Barrier properties** PVC requires the addition of plasticizers to make it useful as a barrier film for flexible packaging. The plasticizers increase chain flexibility and reduce the processing temperature of PVC. For example, addition of 40 vol% dioctyl phthalate plasticizer reduces the $T_g$ of PVC from 100°C to about 5°C. The increase in chain flexibility of plasticized PVC also results in a reduction in its gas barrier properties primarily as a result of higher diffusion coefficients in plasticized films. Table 16 shows the oxygen transmission and water vapor absorption of rigid and plasticized PVC and other polymer materials.
### Table 16. Oxygen Transmission and Water Vapor Absorption of PVC and Other Plastics

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Thickness (µm)</th>
<th>Oxygen Transmission (cc/m²/24h) 25°C 45% RH</th>
<th>Water Vapor (g/m²/24h) 38°C 30% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mylar Polyester</td>
<td>12</td>
<td>140</td>
<td>40</td>
</tr>
<tr>
<td>Metalized Mylar (0D3)</td>
<td>12</td>
<td>0.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>PVdC coated polyester</td>
<td>15</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Plain cellulose</td>
<td>22</td>
<td>8-130 dependent on moisture</td>
<td>3,500</td>
</tr>
<tr>
<td>NC coated cellulose</td>
<td>30</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>PVdC coated cellulose</td>
<td>28</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>LDPE</td>
<td>25</td>
<td>8,000</td>
<td>18</td>
</tr>
<tr>
<td>HDPE</td>
<td>25</td>
<td>3,000</td>
<td>9</td>
</tr>
<tr>
<td>EVA</td>
<td>25</td>
<td>10,000</td>
<td>70</td>
</tr>
<tr>
<td>Propafilm C28</td>
<td>28</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Propafilm CR</td>
<td>26</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>Propafilm MG</td>
<td>20</td>
<td>2,200</td>
<td>7</td>
</tr>
<tr>
<td>Propafoil (metallized)</td>
<td>25</td>
<td>100</td>
<td>1.5</td>
</tr>
<tr>
<td>Cast PP</td>
<td>25</td>
<td>4,200</td>
<td>12</td>
</tr>
<tr>
<td>Cast nylon</td>
<td>50</td>
<td>140 + dependent on moisture</td>
<td>35</td>
</tr>
<tr>
<td>Cast nylon 66</td>
<td>30</td>
<td>80 + dependent on moisture</td>
<td>180</td>
</tr>
<tr>
<td>Oriented nylon 6</td>
<td>15</td>
<td>45 dependent on moisture</td>
<td>260</td>
</tr>
<tr>
<td>EVAL F</td>
<td>20</td>
<td>0.2 dependent on moisture</td>
<td>75</td>
</tr>
<tr>
<td>EVAL E</td>
<td>20</td>
<td>1.8 dependent</td>
<td>29</td>
</tr>
<tr>
<td>Plasticized PVC</td>
<td>20</td>
<td>2,000 + dependent on moisture</td>
<td>200+</td>
</tr>
<tr>
<td>Rigid PVC</td>
<td>20</td>
<td>260</td>
<td>60</td>
</tr>
<tr>
<td>Extruded PVC</td>
<td>20</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Oriented polystyrene</td>
<td>25</td>
<td>2,500+</td>
<td>170</td>
</tr>
<tr>
<td>Nitrile barrier resin</td>
<td>20</td>
<td>16</td>
<td>120</td>
</tr>
<tr>
<td>Aluminum foil</td>
<td>9</td>
<td>0 + dependent on pinholes</td>
<td>0 +</td>
</tr>
</tbody>
</table>

**Adhesion properties and printability** of PVC are excellent. These properties are connected with the polarity of the macromolecular structure of the polymer (Table 17).
Table 17. Adhesion properties and printability of PVC and other plastics as a function of structure polarity

<table>
<thead>
<tr>
<th>Structure</th>
<th>Properties</th>
<th>Adhesion properties-Printability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PVC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polycarbonate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>Polar/Amorphous</td>
<td>Thermoplastics</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyesters</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PU</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Epoxy resin</td>
</tr>
<tr>
<td></td>
<td>Thermosets</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyesters</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PU</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Epoxy resin</td>
</tr>
<tr>
<td>Non-polar/Amorphous</td>
<td>Thermoplastics</td>
<td>HDPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LDPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP</td>
</tr>
<tr>
<td></td>
<td>Thermosets</td>
<td>Polyimide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silicon resin</td>
</tr>
</tbody>
</table>

Generally, polar and amorphous structures offer better properties. In contrast, the non-polar and crystalline structure inherently causes difficulty in adhesion and printing, unless the product surface is treated, and the effectiveness of such surface treatment is comparatively low. Table 17 shows the adhesion and printing properties of major plastics.
**Specific gravity** of pure PVC is about 1.4, which is comparatively heavy among plastics, as is the case for PET. This can be a disadvantage depending on the application.

Table 18. Specific gravity of PVC and other plastics

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>0.91 ~ 0.93</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.94 ~ 0.97</td>
</tr>
<tr>
<td>PP</td>
<td>0.90 ~ 0.91</td>
</tr>
<tr>
<td>PS</td>
<td>1.04 ~ 1.07</td>
</tr>
<tr>
<td>PVC</td>
<td>1.35 ~ 1.45</td>
</tr>
<tr>
<td>ABS</td>
<td>0.99 ~ 1.10</td>
</tr>
<tr>
<td>Polyester</td>
<td>1.38 ~ 1.39</td>
</tr>
<tr>
<td>PC</td>
<td>1.2</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>1.13 ~ 1.15</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.1 ~ 2.2</td>
</tr>
</tbody>
</table>

Source: “Polymer dictionary” by Taiseisha Co., Ltd (1970)

By taking advantage of the fact that PVC does not float in water, it is used in water sealing sheets for agricultural water reservoir or swimming pools, or lining materials for rivers. Regarding flexible PVC products, the specific gravity falls within the 1.1~1.3 range depending on the amount of plasticizer used, which is slightly lower than that of rigid PVC.

In Table 19 is reported a list of properties of flexible (plasticized) PVC and, since the range of physical properties varies widely, depending on the plasticizer content, a guide properties typical of a plasticizer content of 50 phr are given.
Table 19. Properties of flexible PVC with a plasticizer content of 50 phr

<table>
<thead>
<tr>
<th>Property</th>
<th>Test</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, MPa</td>
<td>BS 2782.320A</td>
<td>7.5-30</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>BS 2782.320A</td>
<td>140-400</td>
</tr>
<tr>
<td>BS Softness</td>
<td>BS 2782 365A</td>
<td>5-100</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>ISO R1183</td>
<td>1.19-1.68</td>
</tr>
<tr>
<td>Cold flex temperature, °C</td>
<td>BS 2782 159B</td>
<td>-20 to -60</td>
</tr>
<tr>
<td>Volume of resistivity at 23°C, Ω-cm</td>
<td>BS 2782 202A</td>
<td>10^{10} - 10^{15}</td>
</tr>
<tr>
<td>Aging resistance</td>
<td>Field experience</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

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