Thermoplastic composites are composites that utilize a thermoplastic polymer as a matrix with a reinforcement matrix that can consist of another polymer, glass, carbon, metal, bio-based materials, etc. Approaches to manufacturing thermoplastic composites are not a simple task. High processing temperatures, high melt viscosity, and the lack of drape and tack of prepregs (preimpregnated fibers) are complications that occur during processing. Other factors such as softening temperature, thermal stability, size and shape should be taken into consideration when choosing a processing method.

This chapter will explore conventional techniques used in the manufacturing of thermoplastics composites. Advantages and disadvantages of processing will be discussed as well as the basic processing steps. An overview of the more common approaches will be reviewed and less common techniques will be examined in more detail. Note that even though every single processing method will not be discussed, techniques for creating a composite can be mixed and matched for desired end product.

1.1 Background

Government agencies, aircraft companies, and material suppliers invested hundreds of millions of dollars for thermoplastic research in the 80s and 90s. Today, continuous thermoplastics composites are utilized in only a handful of applications including but not limited to commercial and government aircraft. Thermoplastics represent 80 percent of the entire market, but thermoplastic composites only represent 20 percent of material used in the current market.

Composites are classified as being thermosets or thermoplastics. Thermosets require a crosslinking chemical reaction in order to solidify. Thermoplastics do not have crosslinks; hence, they are essentially stronger than thermosets and can be easily reprocessed.

An amorphous structure of a thermoplastic has a number of intertwined chains. These bonds are connected through covalent bonding but the bonds between the chains are weaker. These weaker bonds allow for the chains to
slide past each other when the polymer has been plasticized and contribute to better elongation and toughness properties. In a semi-crystalline structure, crystallites or tightly folded chains that are connected with the amorphous regions of the thermoplastic. A semi-crystalline also account for 20-30 percent of the thermoplastic composite and contributes to the plasticizing effect of a polymer. The semi-crystalline and amorphous structure contributes to the overall properties exhibited by the thermoplastic composite.

1.1.1 Advantages and Disadvantages

Longer shelf life, shorter processing times, and the ability to be reprocessed and/or replasticized are all benefits of thermoplastic composites. Compared to thermosets, the shelf life of a composite is extended once it has been processed and the processing time is only minutes compared to the hours it can take for a thermoset. Thermosets need extra time to allow the polymerization of the polymer to transpire, which occurs before the thermoset is processed. Thermoplastics have the ability to be reprocessed but the frequency of reprocessing is dependent on the type of reinforcement in the matrix (i.e. polymer vs. glass or biomaterials). Composites can also be reprocessed to eradicate voids within the materials. 

Some disadvantages of thermoplastic composites include high melting viscosity, high processing temperatures, and difficulty of fiber wet out. Since thermoplastics have very high molecular weights, this causes the material to have a high glass transition temperature (T_g) and subsequently a high melting viscosity. The high melting viscosity results in a shear thinning rheological effect on the material and prevents easy fiber wet-out. For some polymers, the T_g is near the degradation temperature which can cause for the impregnation of the fibers to be somewhat difficult with increased complexity of not physically damaging the fibers. Increasing the temperature triggers degradation to occur at a faster rate. Another possible solution to wetting out the fibers is to dissolve the thermoplastic resin. If the polymer resin was diluted to reduce the viscosity, it could then facilitate fiber wet-out but this idea is discouraged because of the cost and issues with the use and removal of the solvent. Also, most high performance thermoplastic composites are not dissolvable in any solvent and would most likely interfere with the reinforcement fiber.

Another disadvantage includes the lack of tack and drape of the prepregs. When trying to lay-up prepreg plies onto a contour shape, difficulty arises. To overcome this boundary, innovative research is currently being performed and is discussed in the following sections.
1.2 Thermoplastic Composite Fabrication Processes

There are several elementary steps to processing polymers in which the goal is to produce flow. When the polymer molecules slide past each other, flow occurs. When the temperature is cooled below the flow temperature, the polymer solidifies and shapes are formed. The tasks of thermoplastic flow, forming, and solidification can be accomplished in a number of ways. Molding, extrusion, spinning, calendaring, and coating are the more traditional methods for processing thermoplastics. Processing techniques are tailored to the fabrication of engineering or a high performance thermoplastic composite. The difference between them is mainly the applications that they are used for. On the other hand, processing techniques will also produce composites in the form of either a laminar or reinforced composite.

Composites that are comprised of different materials (i.e. polymer-metal, polymer-fiber, or polymer-polymer) are called laminar composites. Each layer is then bonded to the next layer to create composite and these individual layers contribute to a different property that is distinctive to that composite. Reinforced composites are comprised of high strength additives such as glass, carbon, biomaterials, or fibers that are assorted within the polymer resin. Note, laminar composites can also have additives.

When integrating composites together, there are various approaches to creating a composite structure. The additives added, whether arranged in a laminar or reinforced manner, can be continuous or discontinuous; orientated or disorientated; or preimpregnated or non-preimpregnated.

1.2.1 Treatment of Fibers

Generally, fiber treatment promotes good interfacial adhesion between the fiber and the thermoplastic resin depending on the type of fiber chosen and the nature of the thermoplastic resin. These operations often occur during the time of the fabrication process mainly because it reduces the handling of the fibers.

Prepregs are reinforcement materials that are preimpregnated into a thermoplastic resin matrix which can be woven or uni-directional. When creating prepregs, processing temperatures are need to be taken into account because some fibers will degrade at that state. Common prepregs fibers include but are not limited to glass, carbon, aramid fibers, or other thermoplastic resins. The length of these fibers (i.e. short or long) can contribute to the overall properties of the composite.
1.2.2 Traditional Polymer Processing Fabrication Methods

1.2.2.1 Extrusion

An extruder is the most widely used method for processing plastic and plastic applications. This allows for a material to be extruded in a uniform cross sectional area through a die. The material is propelled through barrel via the hopper and goes through 3 main sections of the barrel where the material is mixed, compressed, and metered through the die. An extruder can also be useful in the mixing of fiber reinforced thermoplastic composites. A detail explanation of the extrusion process will be given in chapter 12.

1.2.2.2 Injection Molding

A thermoplastic polymer is heated within a cylindrical chamber to a temperature that causes the material to flow. Under heat and pressure, the molten material then flows to fill a mould at the end of the chamber. The material is hydraulically pressed from the chamber to a relatively cold mould through a plunger or ram. Is is then compressed and melted by a screw that moves forward and backward. Once the screw moves backward, it is ready for the next cycle of material and the plastic mould is ready to be removed. More details about this process will be given in chapter 13.

1.2.3 Consolidation

Consolidation is the process of flattening out individual prepreg layers and forming a bond between them. Volatiles are squeezed from the laminate but voids can be established through the entrapment of air, moisture, and solvents. The consolidation process, shown in figure 1, consists of the heating, consolidation, and cooling phases in the creation of a composite. Since the time required for a chemical reaction is irrelevant, the time needed to reach the consolidation temperature is a function of the heating method chosen. This is also dependent on the specific thermoplastic resin. However, time needed for consolidation is dependent on the product dimensions desired. Pressure should remain constant until the temperature falls below the melting temperature ($T_m$). In result, the nucleation of voids are limited, elastic recovery of the fiber bed is suppressed, and desired dimensions are maintained. ²
Consolidation can occur in a number of processes including prepreg layup, pultrusion, tape laying, or tow placement. Also, the wetting of the fibers is achieved during consolidation. The composites themselves are then fabricated in two stages: prepregging/pretreatment and consolidation.

1.2.3.1 Tape Laying/Tow Placement

Tape laying and tow placement, shown in figure 2, are both film stacking methods. Prepreg layers are incrementally and continuously consolidated together to create a composite. At the entry of the roller region, the nip point is formed by the heating of the incoming tow and substrate layer which is formed by previously laid and consolidated tows/tapes. Bonding takes place under the roller and the structure appears to be ready. The rollers, supply spool (of prepregs), and heating source (i.e. hot gas torch) are mounted on a common frame called the tow placement head. The prepregs possess the full rigidity after polymerization but not enough drape to be laid against contour shapes. In result, they are laid as a flat panel and then molded into the desired 3-D shape. Using woven fabrics can assist with the difficulties of creating 3-D shapes. They can be used to produce partial geometries with intricate features but are particularly better suited for the fabrication of larger structures such as aircraft wing skins.
Tape laying and tow placement differ in the size of prepregs used but are based on the same principle, fusion bonding. Fusion bonding is the application of heat and pressure at the interface of two layers, in this case the thermoplastic prepregs in contact. Cooling occurs at the interface and a bonded product is then produced, illustrated in figure 3. Autohesion or healing is initiated by the elevated temperatures and softens the interface. The pressure is a mode of flattening the interfacial stringencies and can be referred to as the intimate contact process. 

1.2.3.2 Pultrusion

Pultrusion is another continuous composite processing method that integrates reinforcement impregnation with composite consolidation. The reinforced fibers (in the form of tape, woven, and/or mat) are driven through a thermoplastic resin bath. This bath impregnates the resin, drives it through a preforming guide system, and then through the pultrusion die. As it passes through the system, the composite is heated,
shaped and formed. A pulling system is used to control the process speed as well as create a dragging force on the material. Finally, a sawing system is used to cut the finished product. A schematic of the process is shown in figure 4. More details about the pultrusion will be discussed in Chapter 2.

1.2.4 Filament Winding
Filament Winding is a continuous process in which fibers are wound around a rotating core or the mandrel. The fiber spools are mounted to a creel and then fed through an alignment device to create a band of fibers. The fibers can be wrapped in either a hoop winding, helical, or longitudinal direction and can be wrapped successfully to each other. The tension over the mandrel creates a positive pressure and compacts or cures the laminate. To avoid some issues created by filament winding, the use of prepregs is an alternative. A schematic of the process is displayed in figure 5 and will be further discussed in chapter 7.
1.2.5 Joining

The methods utilized for joining thermoset based composites can also be used for joining thermoplastic based composites. Joining is a bonding technique that is also based on the application of fusion bonding. Such techniques can include melt fusion, heated tool welding, ultrasonic welding, or conventional adhesive bonding. Joining is preferably used when loads are very high or a high level of reliability is required. Thermoplastics inert and nonpolar surfaces allow for better adhesion bonding to other materials. The topic will also be discussed further in chapter 14.

1.2.5.1 Mechanical Fastening

Mechanical fastening is a multi-step operation that requires no surface preparation step and it is distinguished by the cut out (hole) required for fastening. For thermoplastics, an initial concern was that the material would creep, therefore causing the loss in strength and the fastener. When a hole is placed in a composite, stress concentrations are created and the overall loading on that bearing is reduced. Joining of thermoplastic composites exhibit the same basic failure modes of metals but behave the same as thermosets which is the traditional material used in the process.

Mechanical Fastening is one of the more difficult fabrication processes resulting in the composite becoming more susceptible to damage. Compatibility between the thermoplastic composites is important. Materials should be chosen based on corrosion abilities,
strength, joining configuration, and type of fasteners applicable. Modes of failure should also be considered.

1.2.5.1 Melt Fusion
As previously discussed, thermoplastic composites surface chemistry and physical characteristics allow for reprocessing and good adhesion properties. The thermoplastic resin can then be placed over a bond line to increase the bond of the composite. However, if the joint is centrally located within the composite, adequate pressure measures need to be carried out. Additional pressure precautions prevent elasticity and delamination of the plys at the interface.

1.7 Conclusion
Thermoplastic composites are composed of a thermoplastic polymer matrix reinforced with another polymer, fiber, or material. The nature of the composite’s matrix and reinforcing material distinguishes which processing method should be used. Traditional processing methods such as extrusion and injection molding can be utilized in the fabrication of a composite; but other processes like consolidation, prepregging, and joining are more innate with the special characteristics of a thermoplastic composite. When details about specific features and properties are known of a thermoplastic composite, processing and fabrication proceedings are less complicated.

References


2

Pultrusion

By Carole AUTORI

The term “pultrusion” is the combination of the words “pull” and “extrusion”. Over the last 70 years, this process has experienced significant improvement and is nowadays one of the most cost efficient methods for production of composite materials having constant cross-sectional profiles. This continuous processing technique for molding composites offers the formation of high-quality-engineering-industrial products which have close dimensional requirement. A common example is the pultruded rods used as reinforcement in the concrete elements in the construction industry. This is a single-step process where the composite is manufactured and molded at the same time. Both standard and special-purpose molds exist and give the resulting product a constant cross-section.

In this chapter, an attempt will be made to describe the pultrusion process, and its applications. Complete and detailed information can be found in Reference 1.

2.1 Background

In the 1950s, Sir Brandt Goldsworthy, one of the pioneers of the pultrusion process, contributed to the development and improvement of the machines and tools used in pultrusion from a simple composite manufacturing process to a marketable way of production. Pultrusion was then only used in particular sectors, such as the civil-engineering infrastructure sector, where constant cross-sectional materials that should have structural capability and close dimensional tolerance were required. The pultruded parts were often on standard shapes with longitudinal continuous fiber placement in a glass matrix. Three thermoset resins were available at this time - unsaturated polyester, vinyl ester and epoxy resins – whereas glass fibers were often used as reinforcements. Unlike the current machines, the early ones had a vertical design and had often an intermittent pull type.
Later, in the 1960s, the need for pultruded sections in various market applications – such as production of channels and related products, use of composite in infrastructure where metals cannot be used - pushed the industry to invest capital in the fabrication technique, leading to an improvement of the machines and tools as well as a diversification of reinforcement and matrix. The United States has been and remains at the heart of these major developments.

Unlike many other manufacturing processes, these developments were not the outcome of the US governmental research. Pultrusion was indeed regarded as “a low level of manufacturing” compared to other processes such as tape-laying, filament or filament winding that were more suitable for defense applications. However, industries that decided to invest in this method, as well as customers, leveraged the pultrusion technique by improving and building a reputation to the process. For example, pultruded components were chosen for their light weight, corrosion resistance, electrical insulation, high-strength, long life and low-maintenance requirement.

In the 1970s and 1980s, the technique was improved thanks to the parallel development of the filament-winding technique and the introduction of reinforcement varieties such as Phenolic systems and modified acrylic resin – often named “Modar”. The sophistication of the pultrusion method lead to the diversification of size and shape of the profile molds. Special “custom-molded” profiles could be designed in order to meet a customer’s particular needs and performance requirements.

Nowadays, research on resin curing thanks to modelisation, use of new resins, improvement in tool and machine fabrication as well as an increasing need in high performance composite profiles in a wide range of applications have also promoted this method as one of the most cost effective processing methods for composites.

The table below lists the advantages and limits of the pultrusion process.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Cost-effectiveness at high productivity</td>
<td>- High investment needed: expensive shaped molds, tools and machines</td>
</tr>
<tr>
<td>- Excellent mechanical, physical and environment Resistance properties of the pultruded composites</td>
<td>- Maintenance of equipment</td>
</tr>
<tr>
<td>- Adjustment of the fiber-matrix couple and of the fiber ratio regarding the desired properties</td>
<td>- Skilled labor required for controlling the complex structural design</td>
</tr>
<tr>
<td>- Large diversity of profiled shapes</td>
<td></td>
</tr>
<tr>
<td>- Production in large or small quantity of the part</td>
<td></td>
</tr>
<tr>
<td>- Low labor content</td>
<td></td>
</tr>
<tr>
<td>- High raw material conversion efficiency</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2.1
Advantages and limits of the pultrusion process
2.2 Applications

Nowadays, pultrusion is well-established in the world composite market-place and various applications are using pultruded composite components. They can offer unique properties combining the excellent properties from the component materials (mechanical or chemical properties for example) and good structural properties from the pultrusion manufacturing process. Moreover, pultrusion is preferred when strict dimensional requirements are needed.

Table 1.2 lists below examples of different applications of pultruded profiles as well as their required properties (from both the composite properties as well as its processing).

<table>
<thead>
<tr>
<th>Desired properties coming from the composite</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction</td>
<td></td>
</tr>
<tr>
<td>Light weight, high strength, fatigue resistance, ease of installation, fire performance, easy maintenance</td>
<td>Flooring and walling systems, fences, bridge</td>
</tr>
<tr>
<td>Excellent corrosion resistance, Suitable for a wide range of environments</td>
<td>Walkways, ladders, staging, fencing, stairs</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td></td>
</tr>
<tr>
<td>Electrical applications</td>
<td></td>
</tr>
<tr>
<td>Insulating properties</td>
<td>Cable tray support members, ladders, transmission poles, towers</td>
</tr>
<tr>
<td>Marine</td>
<td></td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>Wastewater treatment plants</td>
</tr>
<tr>
<td>Light weight, electrical and environmental resistance, cost-effective</td>
<td>Railways, vehicle body panels</td>
</tr>
<tr>
<td>Transportation</td>
<td></td>
</tr>
<tr>
<td>Light weight, easy installation, corrosion resistance</td>
<td>Hockey sticks, ski poles, golf clubs, arrows, kites, sail mats, etc.</td>
</tr>
</tbody>
</table>

**TABLE 2.2**
Examples of applications of pultruded composites [12] [1]

2.3 Processing

The pultrusion process is a simple process which allows for the fabrication of continuous length composites to the desired close dimensional cross-sections.
In this section, the process will be explained. This includes a description of the machines and tools used as well as explanations of the different steps of the process.

2.3.1 Overview of processing

![Figure 2.1](image)

**FIGURE 2.1**
Typical production line [8]

Figure 1.1 shows an example of the pultrusion process line. First, strands or plies of the reinforcement fibers are pulled continuously through a bath filled with the desired liquid matrix resin. The pre-impregnated fibers are then gathered gradually into a preformed shape and enter in a heating die.

In the heating die, the polymerization of the resin occurs resulting in the cross-linking of the polymer resin. By moving forward through the die, the composite part gradually cures and becomes solid. Upon exiting the die, the composite is fully shaped into a solid profile. It is then cooled down. Finally, a saw cuts the product into the desired length. The cut parts are then handled by a take-off system.

The line speed offered by pultrusion is the one of the highest of all of the composite manufacturing processes. The average speed line is 1 m/min for thermoset resins but can be up to sixty meters per minute when using a thermoplastic matrix.

The speed line must be carefully chosen, considering the fiber ratio, the profile geometry, the quantity produced, the final properties of the pultruded composite, the reactivity of the fiber-resin system and the impregnation speed. It will have an impact on the resin wetting of the fibers, the degree of cure and thus on the reproducibility of the desired physical and mechanical properties.
2.3.2 Materials used in the pultrusion process

2.3.2.1 Reinforcement material

Reinforcements are often chosen for their load-bearing performance and their processability but also for their functional properties (electrical, thermal, etc.). The type of fibers, the fiber shape and the thickness of the ply will be important when establishing the set up of the pultrusion line.

Type of fibers

The fibers which are used most often are fiberglass (> 95%). Carbon fibers and Aramid fibers are also often used but are more expensive. Finally, Hybrid, Boron and other organic and inorganic fibers are also used in the pultrusion process.

Note: in pultrusion, the fiber roving is often called the “cheese”

Shape

Different shapes of reinforcement can be used. For example, roving can be used when only unidirectional strength is required whereas mats and fabric forms are preferred when the profile needs transversal strength. More complex shapes such as stitched complexes, tissues, papers and surfacing veils produce a better surface finish for the profile, resulting in a better environmental and chemical resistance for the part. Moreover, prepregs can also be used when a thermoplastic matrix is used [7].

Fiber volume

This parameter will affect the efficiency of the fiber wetting during the impregnation step. For example, a high fiber volume fraction can result in poor resin impregnation in the center of the profile [4].

Thickness of the ply

This has an impact on the die pressure during processing. The thicker is the reinforcement, the higher the pressure applied.
2.3.2.2 Resin material

Resins will be chosen based on the processing and the end-use performance of the profile.

Viscosity, reactivity, working time, cure conditions, dimensional shrinkage, structural performance, chemical and UV resistance, health, safety and environmental aspects are some of the characteristics which will impact on the resin choice.

For the same resin, different grades exist. They have in general different properties such as viscosity, toughness or chemical resistance.

**Polyester Resins**

Unsaturated Polyester Resins (USPE) are the most widely used. Their properties such as low viscosity and high polymerization reactivity are suitable with the processing requirements. Unlike other resins, a high filler content can be easily added in order to change the composite properties and thus meet the customer’s requirements.

Isophthalic Polyester Resins are used when faster production speeds are required. Their cure is more complete than for other resins, especially than those of the Vinyl Ester Resins.

**Vinyl Ester Resins**

Vinyl Ester Resins show an enhanced toughness. They have also better caustic and chemical resistance but they are also more expensive. Typical resins are: Epoxy Vinyl Esters (used for their corrosion resistance), Bisphenol A based resins, Novolak and Urethane Vinyl Ester Resins (used for their lower viscosity).

**Thermoset Resins**

Thermoset Resins are chosen for their low viscosity, low shrinkage, and good mechanical, chemical, and adhesive properties.

Epoxy resins, such as liquid BPA-based resins or Modified BPA-based systems, are used in high performance applications. They have the highest level of toughness, good fatigue and creep performance, solvent, chemical and electrical resistance and their properties remain outstanding at high temperatures. No by-product is formed during polymerization.

Acrylic Resins are used for the high-quality of their surface finish and their fire retardancy. It is possible to add a high percentage of mineral fillers
in Acrylic Resins. Modar is the most commonly known and used type of resins.

Phenol resins are the oldest known resin systems. They have an outstanding resistance to heat and fire and very low smoke toxicity. Consequently, they are used in chemical plants, mining installations and high-risk-to-life infrastructure such as underground infrastructure. Their mechanical properties are similar to those of Polyesters and Vinyl Esters Resins. However, the inherent dark brown color of the cured resin requires a post-curing of the part as the profile surfaces need to be painted. Moreover, this resin is not compatible with all kinds of fiberglass.

**Thermoplastic Resins**

Nowadays, the use of thermoplastic resins is growing. They were often disregarded in the past due to their poor ability to wet the fibers [7]. However, unlike thermosets resins, thermoplastic resins can be remelted and thus post-formed or joined to other profiles. Moreover, they are fully polymerized from the start and no further chemical reactions occur within the die. Indeed, the resin is just melted in order to be shaped to the desired profile. Thus, faster production speed can be reached.

Examples of thermoplastic resins are PEEK, Polyphenylene sulphide, ISOPLAST, and thermoplastic polyurethane.

<table>
<thead>
<tr>
<th>Property</th>
<th>Polyester</th>
<th>Vinyl ester</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.13</td>
<td>1.12</td>
<td>1.28</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>77</td>
<td>81</td>
<td>76</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>123</td>
<td>138</td>
<td>115</td>
</tr>
<tr>
<td>Flexural modulus (GPa)</td>
<td>2.96</td>
<td>3.72</td>
<td>3.24</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>4.5</td>
<td>5.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Heat distortion temperature (ºC)</td>
<td>71</td>
<td>104</td>
<td>165</td>
</tr>
</tbody>
</table>

**TABLE 2.3**
Typical thermoset matrix resin properties [1]

The process dynamics will differ from one resin to the other. For example, there are differences in the gel zone, variation in the gel state for a similar level of cure conversion and variation in volume change when curing between two resins. Epoxy resins are often considered as the most challenging.

These effects need to be controlled in order to produce high-quality products. For example, the pulling forces can be adjusted regarding the
volumetric cure shrinkage or the viscosity of the resin. If not, blistering, voids and/or cracks [5] can be generated on the parts.

**Additives**

Additives can be added to neat resins in order to enhance their mechanical, chemical or functional properties. Thus, low profile additives are chosen for improving the surface finish of the part. Fillers are often a solution for creating more cost-efficient resins. They can also reduce the exothermal temperature as the resin polymerizes, improve the interlaminar shear property and the fire retardancy of the matrix as well as changing its electrical properties. Pigments can change the surface color and appearance of the product and could sometimes act as filler.

Another key role of additives is their impact on the processability of the resin. When chosen correctly, they can reduce frictional forces between the pultruded profile and the die mold. In fact, resins are chosen for their good adhesion properties and will therefore bond to the internal surfaces of the die (this is known as degradation of the die and of the pultruded profile, a higher force needed to pull the profile through the die). A release agent is often used for fixing this issue.

Additives can also be used for controlling the shrinkage properties of the resin. When the resin shrinks during curing within the die, an air gap is formed at the die-profile interface leading to a less efficient heat transfer. This will affect the curing of the part as well as other process parameters (pulling force, pressure within the die, etc.) [3]. Additives can then be used to control the shrinkage level of the resin.

However, all these additives can also act as abrasives and thus can lead to the damage of both the composite and the machines. As a consequence, the type of additive and its weight/volume percentage need to be chosen carefully.

### 2.3.3 Machine and process detail

The pultrusion line is usually made of six distinct regions which are bolted together to form the complete system. As only few pultrusion manufacturers use thermoplastic resins, components of a typical production line for thermoset resins will be described further in this section.

Its overall length is rarely less than 12m and can be 18m long or longer. Space between the individual units can be left in order to add or remove machines for other in-line process operations as and when required.
2.3.3.1 The creel rack

The reinforcement is stored at the start of the pultrusion line, usually in the form of rovings. These rolls are the creel rack. They will feed the rest of the line with reinforcement. The creel racks can be horizontal or vertical and rotating spindles carry out the reinforcement distribution.

Different systems of reinforcement guidance exist. Some of them are tailor-made for a particular type of reinforcement or fiber as they can result in tension on the fibers if they are not chosen properly. For example, carbon fibers are particularly sensitive to this issue.

The creel racks are usually large and are designed to be mobile. Thus, they are often equipped with wheels and can be changed quickly when a new rack is needed.

2.3.3.2 The impregnation bath

The impregnation of the resin with the reinforcement is an important step of the process. When it is well controlled, an optimum reinforcement to resin ratio can be reached leading to better physical and mechanical properties of the composite. Any resin additive should be added at this stage of the process.

Three major techniques can be used:

- **Wet-bath technique**: the reinforcement is immersed in a bath filled with resin. It is the cheapest technique to install and to operate. Resin levels can be controlled manually or automatically as a constant resin level can help the wet-out efficiency.

![FIGURE 2.2](image-url) Wet-bath technique [1]
- **Dip-bath technique**: use of bars submerged with resin. An assembly of several dipper units is often used in industry. This technique is preferred for higher viscosity resins as they allow a better impregnation of the fibers. However, the friction forces are also higher.

- **Through-bath technique**: the reinforcement goes through a bath where guidance plates were installed. The reinforcement goes through holes which were made in these plates. This technique is preferred for reinforcement that is more prone to breakage.

The resin can also be directly injected into the die. This method is the most environmentally-friendly and this technique is more and more commonly used. However, this method often results in a poor fiber wetting and leads to the formation of defects such as blisters [5].

![Resin injection die](image)

**FIGURE 2.3**
Resin injection die [1]

The type of bath, its temperature and its distance from the die entry must also be controlled based on the resin cure properties (speed of curing, viscosity, etc.)

Moreover, the method should be chosen considering the type of reinforcement (shape and material) as well as the thickness of the ply, as these factors will have an impact on the efficiency of impregnation.

Note: The impregnated fibers are often called the “pack”.

### 2.3.3.3 Reinforcement guidance

Once the reinforcement is surrounded by the resin, it will be gathered together and pre-shaped before entering the die by using reinforcement guidance. In general, the preform plates are bigger than the actual size of the die [6]. The key point is to provide an optimum distribution and packing of the reinforcement pack. Thus, the larger the profile the more complex the reinforcement, the more important this step is. A balanced profile
construction and symmetry are often required in the guide design. The mechanical properties of the pultruded shape will depend on the parallel alignment of the fibers.

For example, when using unidirectional roving fibers, the reinforcement can go through small holes made in two or three successive plates. The plates are usually made of steel, Teflon or Polyethylene. The guidance will give a shape to the pack meanwhile removing the excess resin around the reinforcement.

2.3.3.4 Heating die

This component is the most complex part of the pultrusion line. The material used for the die, its design and its heating process will have heavy impacts on the profile processing.

The die is usually made of two pieces which create a parallel cavity when fit together. When sliding into the cavity, the reinforcement pack will be heated resulting in the curing of the resin (going from a liquid to a solid state). This induces friction forces along both upper and lower tool-halves.

Die materials

The die materials will impact on the life time of the die. Suitable tool steels are preferred as they offer good mechanical properties and are suitable for the refurbishing process of the plates. Both the upper and lower surfaces of the die are usually hard-chrome-plated and diamond polished for an increase in wear resistance and a reduction in die friction. The choice of plate is crucial as the plate surface can be removed by the pack if there is not good adhesion between the plate and the die. An alternative is to use steel with a high chromium content. However, it is important to note that too hard a metal cannot be used, as the die is subject to high and cyclic physical and thermal stresses and could crack more easily.

If the material selected impacts the duration of the die, it will also impact the upkeep of the cavity. Depending on the type of reinforcement, both surfaces need to be re-polished or re-plated every 30 000-50 000 meters of manufactured profile. In addition, the size of the die is often limited by the tool shop surface grinding machine and is usually one meter long.

Wear occurs at two preferential locations: one point at entry and another point that is usually one third of the length (where the resin polymerizes). Thus, in order to reduce maintenance costs, symmetric designs of the die can double its life by exchanging the entry and exit points.
Importance of die design

By controlling the manufacturing process of the die, an optimum die design can be reached and thus enhance the production of better pultruded profiles.

The first rule is to avoid sharp corners in the die, as resin can cure and fill these areas as there is no abrasive removal in these corners.

In addition, the resin shrinkage during polymerization must be taken into account. Each resin behaves differently, which can be influenced by the type, the orientation and the fiber volume of the reinforcement. By using proper dimensional calculation, the volume change of the pack can be predicted and the die design can allow the shrinkage of the part while producing the profile with the required dimensions. This is important as pultrusion is often used for the production of parts with close dimensional requirements. The Pultrusion Council of the Composites Industry and the European Pultrusion Technology Association (EPTA) established standard dimensional tolerances which are used in industry and accepted by authorities such as the American Society for Testing Materials.

Then, pultruded materials sometimes need to have post treatments because of visible longitudinal lines on the outer surface of the profile. They cannot be avoided but the design of the tool can be changed in order to change the location of these ribs.

Die designs are usually made of two halves forming a cavity when fit together. There can be one or several cavities following each other. The number of cavities will strongly impact the final pultruded parts. Companies are often divided on this subject.

It is finally worth noting that a good die design will induce a controlled heat flow within the cavity, optimally curing the composite.
**Die profile**

Die profiles can be classified as standard or custom. “Standard” designs are those widely used by pultrusion companies around the world. For example, bar, hollow, rectangular, round, channel, angle, I and H-sections are considered to be standard profiles. An internationally recognized classification system has been created by the pultrusion industry for optimal die selection. The system is based on a six or more alphanumeric code where the position of each would have a particular significance. [12]

On the other hand, custom profiles are designed and manufactured for a particular customer. A very close relationship between the manufacturer and customer is vital at every stage for the design of the die and specification of a custom molded profile. They should discuss the choice of resin and reinforcement, the choice of additives, the geometry and dimensional tolerances of the profile, the final properties of the part, the production rates, the part-to-part reproducibility, the surface finish, the appearance, the durability and the last of the die. The adequate tools must also be owned by the customer.

**FIGURE 2.5**
Examples of standard profiles [1]
**Die mounting**

The die needs to be mounted properly and manufacturers should be able to remove it efficiently for maintenance purposes. As this part can be challenging, it will not be discussed further in this review but more information can be found in Reference [1].

**Die heating**

This step deals with the control of heat flow and its distribution through the whole die assembly in order to optimizing the resin curing. The degree and uniformity of a cure can considerably influence the mechanical properties of the product [2]. This step is even more challenging as the resins exhibit a very low thermal conductivity [5]. Finite element analysis is nowadays often used for modeling the various aspects of the heating process: temperature control, position of the heaters, effect of exothermal reaction, symmetric/asymmetric shape of the die, depth of the section, performance required, etc. Articles can be easily found in the literature regarding this topic such as References [2] through [8]. Their goal is to find various models of the complex and still not clearly defined curing process within the die. Reference [2] developed a mathematical model whereas Reference [3] investigated a thermo-chemical based model for modeling the pultrusion process. They investigate relationships between different process parameters in order to optimize the die-heating environment.

A common way to heat the die is to use platens put in both sides of the die. It is usually heated by one of the three following modes: electrical resistance; hot oil or steam. The first one is the most common and the most convenient technique. It allows a good control of the temperature by using thermostats along the die.

When platens or simple electrical heaters are not used, radio frequency or microwave heating can be used. However, by using these two methods, the control of the heating flux is more difficult due to the absence of sensors with an easy set-up.

**Post-die sizing**

At the die exit, the pultruded profile is mainly solid but still hot. This allows for a post-die “sizing” of the part. For example, a cooled aluminum block can be used to ensure that the whole profile has the correct angularity.
2.3.3.5 Pulling mechanism

The pulling mechanism ensures the continuous and steady motion of the product at a specified speed. The profile is gripped at the die exit and will be pulled by the mechanism. The applied pulling force must take into consideration all the resistance forces built up during the previous steps described above (resin viscosity, friction forces in the cavity, die surface condition, thermal expansions, complexity of the profile etc.). There are multiple effects and they are often hard to predict. A number of stable parameters can, however, be used in order to choose the most suitable pulling system.

Continuous pulling systems

Two distinct versions of pulling systems are employed:
- Continuous tractor: the profile slides between two surfaces of either a belt-type machine or a cleat-type machine. The first one is used for simple profiles demanding lower pulling whereas the second one is more suitable for larger profiles but sensitive to wear. A major disadvantage of the continuous tractor system is that the clamping force is not homogeneous along the length of the pulling system.
- Reciprocating puller: this more complex system is suitable for larger and more complex profiles. It consists of continuous back and forth movements of two puller units to get the composite in motion.
- Combination of the two is also utilized.

Gripping arrangements

These arrangements are usually found in a reciprocating pultrusion system. They generally consist of two pulling systems. A first one grips the dry profile and pulls it until the end of its stroke before going back to its starting point. The profile is thus repositioned and moves forward thanks to the second puller.

The method and the material used for gripping the profile must be chosen carefully. The grips must prevent the profile from slipping. Slippage of the profile could indeed lead to a final cut at an undesired length. Moreover, the grips must not damage the part by using an excessive clamping force. Finally, the grip material must be able to be used at the designed operating temperatures over a long period.

As a consequence, grips are often made of steel or aluminum and a thick urethane layer is applied on their surface. The urethane has typically a Shore A Hardness between 90 and 95. On the contrary, rubber is not recommended
as black marks can remain on the profile surface. The outer urethane layers can be machined in order to fit with the profile shape or can be left as-received from the supplier.

By using this method, the manufacturer should check the precise alignment of the profile at the die exit. Health and safety regulations must also be taken into account as the gripping system typically works thanks to hydraulic cylinders.

Unlike the continuous pulling systems, the force applied on the profile is homogeneous. This system is also appropriate when processing several profiles at the same time.

![Typical gripping arrangements](image)

**FIGURE 2.6**
Typical gripping arrangements [1]

### 2.3.3.6 Saw cuts

This is the last part of the pultrusion process and is usually moveable in order to add further in-line sections if needed (i.e. powder coating). The cut-off saw is often called “a flying saw” as the saw table is clamped to the part at the beginning of the cut and then moves at the same speed at the pultruded profile when cutting. Once the part is cut, the saw returns to its starting position.

### 2.3.3.7 Take-off systems

Once the profiles have been cut, they need to be supported. For example, a simple flat table can be set just below the saw. More sophisticated take-off systems exist such as roller conveyors.

### 2.3.3.8 Additional on-line processes

Different on-line processes can be added along the pultrusion line when required by the client’s needs. As they add important benefits, they also
demand a great attention. They can be a weak point in the process line and result in frequent and total process shut-down.

One of the most widely-used additional processes is pullwinding. It is often used when the profile is tubular in nature. Several fiber layers are wrapped on a mandrel in order to produce a tube. More information can be found in the reference [1].

Moreover, numerous variants of the production line exist as several methods can be used for one single step. Optional stages can also be added or removed at the typical production line described above and distances between stages can be adapted. For example, when using thermoplastic resins, a cold and a hot die are usually present. A preheater is also located before the first die in order to preheat the prepregs. A cold die ensures the stability of the profile dimensions. More details regarding the production line as well as the process parameters when using thermoplastic resins can be found in Reference [7].

2.4 Quality controls of the final pultruded composites

Even if the pultrusion process is based on simple physical principles, the phenomena occurring during the fabrication of the profile are complex. Manufacturers and clients should control carefully every step of the process. Standards are available in order to ensure good manufacturing and good quality of the profiles [9].

Design controls

These are one of the most important criteria if the industry wants to product successful profiles. Customers and manufacturers should communicate closely in order to find a viable and efficient solution to the precise requirements of the client. They should not neglect this step and should ask an exterior help if they do not have a sufficient knowledge of the pultrusion process. Below is a non-exhaustive list of the crucial points when designing a pultruded profile:

- Geometry of the profile. Customer and pultrusion companies should both approve the proposed profile as some customer’s requests are not always compatible with the pultrusion process or the die
fabrication. For instance, sharp corners or thin section details which might not be reproducible must be avoided. Drafting the die can be helpful during this step.

- **Choices of matrix and reinforcement** Regarding the required specifications but also regarding the geometry and dimensions of the die. Compatibility between the two materials, properties of the final composite and shrinkage of the resin are particularly important in this step and need to be foreseen.

- **Profile thickness**: An increase in the thickness of the profile can enhance its structural capability but it is not always the best solution when using pultrusion. It can lead to a non-uniform curing of the cross-section of the part and thus lower properties of the profile [2]. Moreover, at a particular matrix/reinforcement specification, the maximum production speed can be limited by the profile thickness and consequently the price per unit length will vary per batch.

- **Die cavity**: A constant cross-section over the majority of its length will provide an entire area where the temperature conditions are sufficient to initiate the curing reaction whereas change in the cross-section can lead to a critical modification in the resin curing.

- **Die length**: The longer the die, the better the final results will be. Indeed, it induces more precise temperature zoning and thus can lead to faster process speeds. A typical die has a length of between 900 to 1000mm. With a very high production volume of the part, the die length can reach 1500 mm for economical reasons. On the contrary, shorter dies may be required due to the geometry (better curing control) but in that case, the process speed will be limited.

- **Die material**: The material must handle high temperature conditions, corrosive environments, and pressure due to thermal reactions.

- **Die surface treatments**: The cavity surfaces must show some surface lubricity. For that, surface treatments of the two halves must be applied. Chrome plating is usually used. However, problems of uniformity, adhesion and micro cracks within the plating structure are common. The plating method and the thickness (0.025-0.05 mm) should be discussed in order to find the best balance between
wear, uniformity (and thus better reproducibility of the profile) and cost of the machine.

**Monitoring and data controls**

Most pultrusion machines have control panels. Three main functions can be controlled by the manufacturer: temperature, machine operation and control, and monitoring and data logging.

It is important to understand the process dynamics and reaction kinetics that are governed by the resin’s exothermic reaction as well as the by-products formed during processing. The exothermic reaction of the resin occurs when the pack reaches the temperature at which the reaction can be initiated. The gelation of the resin will also occur at this temperature [3].

![FIGURE 2.7 Die Dynamics and pulling resistance [1]]

The die temperature, the profile cure rate and the line speed are closely related [2]. For instance, the die temperature will affect the curing properties of the resin. As a result, there is an optimal position within the die length where, if the exothermic reaction is initiated at that point, then the rate of polymerization will be optimized. As a result, an optimal speed can be defined for pulling the system. It is important to note that too high speed can lead to the formation of blisters on the surface of pultruded composites. This is a major issue faced by companies when they want to increase their productivity, as discussed in Reference [4].
Thanks to the panel controls, the pressure within the die can be easily controlled. A steady pressure rise within the pack should be applied, allowing a better resin flow through the fibers and decreasing the chance of void formation in the pultruded profile [6]. Unfortunately, the pressure within the die is more complex to predict. [6]

Moreover, quality controls can be performed by the manufacturers through the different steps of the pultrusion process. For example, the raw materials can be controlled when received by the suppliers. Then, the different parts of the pultrusion line can be controlled using the machine control panels and the collected data. The temperature and pressure within the die are, for instance, two key parameters. The manufacturer should communicate the monitored and recorded parameters to the customer such as catalyst addition, release agent percentage, die temperature profile, line speed and pulling force. At the end of the process, the physical and mechanical properties of the finished product can be evaluated. Reference [5] proposed an analysis of the microstructure of the composites in order to have a better understanding of the phenomena occurring within the profile and thus provide efficient changes in the production line. Finally, health and safety regulations should be applied by the manufacturer.

All these quality controls can ensure the production of high-quality pultruded profiles within the different requirements such as the dimensions of the part. Manufacturers who perform these controls often give a Certificate of Compliance to the customer to guarantee the quality of their products. Table 1.4 below shows typical mechanical properties of different pultruded profiles.
<table>
<thead>
<tr>
<th>Glass content (% wt.)</th>
<th>Roving/polyester</th>
<th>Woven roving/polyester</th>
<th>SMC polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.6-2.0</td>
<td>1.5-1.8</td>
<td>1.8-1.85</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>410-1180</td>
<td>230-240</td>
<td>50-90</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>21-41</td>
<td>13-17</td>
<td>9</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>690-1240</td>
<td>200-270</td>
<td>140-210</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>210-480</td>
<td>98-140</td>
<td>240-310</td>
</tr>
</tbody>
</table>

**TABLE 2.4**
Mechanical properties of typical pultruded laminate [1]

**References**


Polymers offer a great deal of versatility and functionality as a result of chemistry and processing conditions. It follows that polymer coatings are used in a great many industries. At its core, the purpose of a polymer in this context is to protect a substrate – a metal, ceramic, composite, or different polymer – from a corrosive, unstable, or otherwise non-ideal environment. There are several strategies for creating a polymer surface. These methods can be either physical (e.g. dip coating) or chemical (e.g. chemical vapor deposition).

One of the reasons polymers are ideal for coating applications is their workability: polymers can be easily shaped at relatively low temperatures compared with metals. In addition, polymers can be engineered to be both tough and flexible, which increases the lifetime of the coating. Lastly, polymers are easily synthesized, and many high-quality coatings can be made inexpensively. Overall, a polymer coating is a great choice, and often a necessity, for many applications.

3.1 Applications

Polymer coatings are a class of surface engineering with many applications. One of the most promising applications of such coatings is in the renewable energy industry, as a coating for photovoltaic solar cells. Other applications in the energy industry include thin films for lithium batteries and fuel cells. These products make use of organic and transparent coatings to enhance optical properties. With an increase in demand for affordable alternative energy, we can expect advances in the efficiency in production of such coatings1.

Another important use for polymer coatings is in the medical devices industry. Many implantable devices require polymer coatings for one of two reasons. First, long-term implants require coatings to protect metal casings or other metal components from the harsh environment of the human body. The immune system reacts to these devices as foreign objects, and polymer coatings can be engineered to lessen an immune response. Second, polymer coatings on medical devices allow for easier mobility2.
The decreasing size of medical devices, and the increasing popularity of laparoscopic surgeries, means that a greater number of devices can be delivered via guidewire through the bloodstream. A coating such as silicone or polytetrafluoroethylene is necessary for easing the guidewire through blood vessels without damaging vessel walls.

In Figure 3.1, a medical guidewire is shown delivering a stent to an artery with atherosclerosis. Although the figure depicts a bare-metal stent, a polymer-coated stent is also a popular choice to treat clogged arteries. The polymer coating contains a drug to prevent restenosis, which is the re-growth of the plaque around the stent. The polymer used in this coating is poly(styrene-b-isobutylene-b-styrene), which releases drug as it degrades. The degradation products are not harmful to the patient, and are carried away in the bloodstream. In a 2010 study, drug-eluting-stents have been shown to reduce the “long-term rate of major adverse cardiac effects compared with [bare-metal stents].”

In electronic applications, polymer coatings can be used for either conducting or insulating circuits. Conductive polymers are engineered by introducing ions, thereby creating an electro-active polymer membrane. A study by Liu showed that actuator devices made with “electro-active polymer membranes and ionic polymer conductor network composite” produced more electromechanical movement. This is in part because the presence of the electro-active polymer membrane increases the surface area of the electrodes, increasing storage of ions in the electrodes and reducing ion diffusion out of the system.

Inversely, polymers can act as insulators in electronic applications, as they generally have a low dielectric constant and can easily be applied to metal wires. In a study by Huang, poly(propylene carbonate) was applied in layers to a through-silicon via (TSV), which is an electrical connection
that passes vertically through a silicon wafer for the purpose of making 3D circuits. The polymer coating was shown to decrease leakage current and reduce the capacitance of the TSV.

Lastly, the aircraft industry makes extensive use of coatings in windows, engines, and other parts. Aircraft windows are made with poly(methyl methacrylate) and are typically coated with a hard, optically transparent polymer film. The coatings used in engines are designed to resist wear and corrosion. Design of the coatings must take UV exposure, sea water, humidity, mechanical loading and temperature cycling into account. Polyurethane-based coatings are the most common for these applications.

### 3.2 Deposition Techniques

Deposition techniques are characterized by the application of polymer precursors or monomers to a substrate. This can be achieved by either chemical or physical means, depending both on the type of coating and type of substrate. Relatively inert species are more easily applied with sputter deposition, while reactive species are applied well with chemical vapor deposition. A species is considered reactive if its surface contains reactive functional groups like aromatic rings or radical cations.

For example, Teflon (polytetrafluoroethylene) coatings are good for non-stick applications. However, Teflon does not easily adhere to a substrate because of its lack of functional groups. Thus, physical vapor deposition is preferable for Teflon application. On the other hand, reactive polymer and substrates are ideal candidates for chemical vapor deposition.

Chemical vapor deposition is known for yielding uniform polymer films. This includes coatings for substrates that possess gaps and steps that must be evenly coated. Since physical vapor deposition cannot apply polymer at some angles, chemical vapor deposition is advantageous in this case. An example of a substrate with very small gaps and steps is a biomedical microelectromechanical systems (bioMEMS) device. These devices are micromachined chips that are implantable, minimally-invasive systems for drug delivery, gene therapy, or blood chemistry tests.

#### 3.2.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is the use of a chemical reaction to deposit a film. The reaction occurs between the gaseous phase of a solid material and a substrate. With polymer chemical deposition, the gaseous reactant is achieved by evaporating or sublimating polymer precursors (monomers), with each precursor in a separate chamber, then transporting the gas to a reaction chamber containing the substrate. The monomers are deposited on the substrate, where they react with functional groups on the
substrate and begin a polymerization reaction. The substrate is held on a cooled surface to prevent reversal of the reaction between the polymer and substrate.

Chemical vapor deposition requires that the coating be volatile enough to be vaporized, yet stable enough to remain on the substrate. Since polymers tend to be heavy molecules, the target coating must be able to be formed from precursor compounds that can be evaporated. Since the precursors form polymer macromolecules on the substrate, there is little risk of evaporation after deposition.

In Figure 3.2, an example of a chemical vapor deposition chamber is shown. This particular setup is used for oxidative CVD in the creation of a coating of poly(ethylenedioxythiophene), or PEDOT, using radical cationic polymerization. The monomer and oxidant are both reacted in the vapor phase. The oxidant is then placed in the same chamber as the substrate, where reaction between the oxidant and substrate creates a radical cation on the surface of the substrate. This radical cation is a highly reactive site that facilitates step-growth of a polymer. After exposure to the oxidant, the monomer is introduced to the chamber to begin polymerization. The polymer coating is formed from the substrate interface up. Because CVD is characterized by coating evenly, it is easy to create coatings with multiple layers by changing the incoming monomers via the flow control box seen in Figure 3.2. After the application of polymer is complete, the excess monomer gas is vacuumed off, a process controlled by the throttling valve.
Besides radical polymerization, polymer coatings can be applied via CVD with plasma deposition polymerization. Since plasma is characterized by its ionized state, plasma-enhanced CVD is used in applications where a conductive or semiconductive polymer coating is desired. Polyperinaphthalene (PPN) is an example of a polymer that can be applied in this fashion. As seen in Figure 3.3\textsuperscript{13}, the structure of PPN resembles a network of aromatic rings.

![FIGURE 3.3](image)
The structure of polyperinaphthalene, or PPN

Unlike many polymers, PPN has a small band gap, which means that the energy difference between the highest occupied molecular orbital (valence band) and the lowest unoccupied molecular orbital (conduction band) is relatively small. This energy difference is a hindrance, but not insurmountable to outer shell electrons. Thus, PPN material is a semiconductor. Generally, polymers have large band gaps, which do not allow electrons to rise to the higher-energy conduction band, and are usually used as insulators.

In the experiment by Yu, gaseous PPN monomers were mixed with an argon carrier gas that contained electrons, ions, and radicals. The gas was then transformed into plasma, wherein the monomers were excited by the electrons, then dissociated by the radicals. The dissociated monomers then diffused to the substrate. They then adsorbed to the substrate surface and began a radical polymerization reaction to form a polymer coating.

### 3.2.2 Sputter Deposition

Sputter deposition is a common method of physical vapor deposition, which is a method of applying a coating without chemical reaction between the coating and substrate. The difference between sputter deposition and chemical vapor deposition is that particles are physically stuck to the substrate by the use of bombarding particles at high velocity, rather than by using chemical bonding.
There are three main components in a sputter deposition apparatus such as the one seen in Figure 3.4\textsuperscript{14}: the inlet for gas, the sputtering target, and the substrate. The gas used in sputter deposition contains metallic ions, which are highly energetic. The ions are bombarded at the sputter target, containing the coating monomers. The ions displace the monomer molecules and, due to their high energy, emit fragments in the plasma phase rather than the gaseous phase. The monomer plasma then forms a film on the substrate.

![Diagram of sputter deposition of nylon 6,6](image)

**FIGURE 3.4**
Diagram of sputter deposition of nylon 6,6

The number of monomers ejected per metallic ion depends on both the target material itself and the experimental setup. The target material may be homogenous, or contain multiple components. The size, volatility, and density of each species affects the chemistry of the coating and the time required to achieve the desired thickness. Experimental design factors to be taken into consideration are the energy contained within the ion, the identity of the ion itself, and the angle at which the ions are bombarded. Although the figure depicts ion gas being applied at a right angle, it is actually more energetically efficient for ions to be bombarded at the target from an oblique angle.

As seen above in Figure 3.4, nylon-6,6 is a polymer coating to be deposited onto a silicon wafer substrate. Although nylon-6,6 contains –NH\textsubscript{2} functional groups, a study by Artemenko\textsuperscript{15} was conducted using sputtering rather than chemical vapor deposition so that nylon-6,6 could be applied to a wide range of substrates. Furthermore, the goal of the study was to retain the amino group functionality in the coating. The reactivity of the polymer coating is important in biological applications, where the amino groups can immobilize biologically active molecules and promote cell growth on the substrate.
3.3 Coating Techniques

Unlike deposition techniques, spin and dip coating techniques are performed with fully-formed polymers rather than precursors. The polymers used are in a liquid phase so viscoelastic properties are of great importance in these methods. These techniques are performed at lower temperatures than deposition techniques since the polymers do not need to be in the gaseous phase.

Spin coating is limited to flat-surface applications. It is easy to perform, and is commonplace in photolithography, antireflection coatings, and dielectric or insulating layers of flat microcircuits.

Dip coating is limited to flat-surface and cylindrical substrates. Dip coating is used for everyday applications like handgrips on tools, as well as medical instruments and electrical equipment. It is a less precise method than any of the previous methods.

3.3.1 Spin Coating

Spin coating is a method for applying a thin polymer coat to a flat surface. Polymer is spread using centripetal force. The viscosity and concentration of the polymer act as “resistance” to spreading which must be counteracted by a high spinning speed.

The method for spin coating is described as four basic stages by the IEEE Components, Packaging, and Manufacturing Technology Society\textsuperscript{16}, and is illustrated in Figure 3.5\textsuperscript{17}:

1. “The polymer is dispensed onto the wafer;
2. “The polymer is spread across the wafer (by spinning at approximately 500 rpm);
3. “The wafer is spun at a higher speed (2000-4000 rpm);
4. “The ‘edge bead’ is removed using a backside wash cycle which causes solvent to curl back over the lip of the wafer and wash off the ‘bead’ that is created due to surface tension at the edge of the wafer”
Spin coating is limited to flat, round wafer substrates like silicon or glass, and the roughness of the substrate must be negligible as compared to the coating thickness. This way, the centripetal force allows the polymer coating to evenly spread in order to coat the entire surface. The coating’s thickness depends on both the polymer itself and the processing conditions. Polymer properties to take into account are viscosity, drying rate, and surface tension. Spin rate, spin time, and fume exhaust volume can all have an impact on the final thickness of the polymer coating, as illustrated in Figure 3.6\textsuperscript{18}.

**FIGURE 3.5**
Spin coating of a flat wafer substrate

**FIGURE 3.6**
Illustration of processing condition trends in relation to film thickness and uniformity.
In order for the spin coating process to be repeatable, the conditions must be replicated precisely. For example, a change in spin rate of 50 rpm can “cause a resulting thickness change of 10%” according to Columbia University. Other factors that must be kept constant are humidity, airflow above the sample, and presence of solvent vapors. Spin coating is performed in a “closed bowl” chamber that allows minimal exhaust and minimizes airflow, as an excessively high exhaust rate can cause streaks in the coating which negatively affect reproducibility.

### 3.3.2 Dip Coating

Like spin coating, dip coating is also a coating technique for flat substrates, though it can also be used for cylindrical applications such as handgrips and coated wires. The thickness of the coating is determined by the viscosity, surface tension, and density of the polymer. Processing conditions that affect the thickness are the speed and angle of the dipped surface. After being dip coated, the polymer must be cured by thermal, UV, or IR exposure. After curing, another dip-coating layer may be added.

Flat surfaces and rigid cylindrical surfaces are dipped individually as illustrated in Figure 3.7. This setup is used in a study by Hu, who used this technique to apply a polymer coating to solar cells to improve their efficiency. The polymer coatings compared were poly(3-hexylthiophene), or P3HT, and [6,6]-phenyl-C₆₁-butyric acid methyl ester, or PCBM. Hu found that chlorobenzene solvent yielded the best drying behavior, with few thickness variations at room temperature. Drying processes below 17°C were found to be too slow, while those above 22°C resulted in uneven drying. The room temperature drying process allowed for self-organization and crystallization of the polymer coating.
Dip coating of flat and rigid cylindrical substrates.

Alternatively, non-rigid surfaces (wires) are dip-coated continuously as in Figure 3.8\textsuperscript{22}. The wire is pulled through the polymer melt, and the polymer coating adheres to the wire due to applied hydrodynamic pressure. The polymer coating is then dried.

Akter\textsuperscript{23} created an experiment to apply a nylon-6,6 coating to a hydrodynamic wire, with variations in temperatures, applied back-pressures, and wire velocity. The concentration and viscosity of the polymer was left unchanged. The study found that the coating was uniform up to a velocity of 12 m/s, and that there was no deformation of the wire. Such a velocity can be appropriate for large-scale industrial applications, making this setup feasible for a larger operation.

The back pressure was found to be important to wire uniformity as well: a lack of back pressure causes less adhesion of the polymer to the wire. The study also found that the polymer began to burn at 230°C. This shows that continuous dip coating is a relatively low-temperature process.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{w-type-dip-coater}
\caption{W-Type Dip Coater}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{one-side-dip-coater}
\caption{One Side Dip Coater}
\end{figure}

Dip coating of wire substrates
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Foaming

by Jianing Cao

Foam, a typical category of engineering materials that have been widely used in different industrial areas, refers to a continuous solid or liquid with uniformly dispersed bubbles inside. Foams usually serve as packaging materials, thermal and electrical insulations or light weight structural components due to their properties like high stiffness and impact resistance, dielectric and thermal resistance, high strength to weight ratio, etc. Along with the development of technology and the growing use of polymer foams in recent decades, the performance of foams has been greatly improved as well as foaming techniques.

Foaming behavior is resulted from dramatic change of the surrounding temperature and pressure. This phenomenon allows gaseous phase to change from its original liquid state to a relatively unstable gaseous state [1]. Spherical bubbles are usually generated since less surface energy is needed to maintain the gaseous state.

Generally, polymer foaming starts with introducing a gaseous phase into a polymer melt. Many methodologies have been developed to incorporate gases into a liquid or a solid and the most commonly used method in polymer foaming process is to blow gas into the polymer melt. Chemicals that have been applied to provide physical blow power are called physical blowing agents (PBAs). Another commonly used type of blowing agents is chemical blowing agents (CBAs). Chemical blowing agents will slowly decompose within the melt and form a gaseous phase. Once the foaming of gaseous phase is completed, the melt must be solidified to seal newly formed cell structures and prevent condensation of bubbles. Otherwise, gaseous bubbles could collapse and change back into their original liquid state which means a failure.

In a dense matrix, the number of gas molecules determines whether or not the gaseous bubbles could successfully transport thoroughly to form a uniform cellular structure [2].

Foaming process can be very different for thermoplastic and thermoset. Since some thermoplastics have thermally reversible characteristics with respect to the introduced gases, the foaming process is heavily dependent on the ability of equipment to control thermal conditions. The manufacturing
process of thermoset foams is more involved with kinetics and composition of blowing agents [3].

### 4.1 Historical Background

In past decades, intensive multi-disciplines research had been done on the topic of polymer foaming. Chemists, material scientists and engineers worked together to develop new processing methods to produce different foaming products to take advantages of properties mentioned in the beginning of this chapter. Although different polymers could greatly influence properties of foams, variable properties provide industry a much wider range of applications.

Starting from first half of 20th century, foaming methods as well as rigid and flexible foams of different plastics like polystyrene, polyurethane and polyethylene have been gradually developed and manufactured [4].

In foaming process, rigid foam means the presence of closed-cells within the foam. The walls or membranes of each cell around gaseous bubble remain intact without any rupture. On the contrary, flexible foam means the existence of open-cells which the walls or membranes ruptured after curing. The typical foaming methods developed during this stage are listed below [5]. Besides these processing methods, another significant issue related to foaming practice is the development of processing equipment.

- extrusion foaming
- injection molding foaming
- bead foaming
- rotational molding foaming
- compression molding foaming
- reactive foaming
- reactive mold foaming

In the 1980s, raised environmental concerns resulted from application of chemicals like carbon dioxide and CFCs in foaming industry had been considered as a negative factor to continue developing more applications of foam materials. Foam industries were pushed to start the selection of alternative blowing agents. This selection process depends not only on the properties of polymers but also properties of foaming agents which will be discussed in the next section [5]. Finally, with great efforts, environmental problems including depletion of ozone layer and green-house effects had been addressed by using hydrocarbons, inert gases, etc. as alternatives.
4.2 Foam Structures and Properties

Foamed materials possess interesting physical and thermal properties that are determined by properties of polymer matrix, properties of foaming agents and the cellular structure. The cellular structure is formed when the gaseous bubbles are liberated and dispersed in polymer matrix. Density, stiffness, impact resistance and thermodynamic properties including specific heat, equilibrium constant and heat conductivity are examples of interesting properties. Some of these properties are mainly governed by the gaseous phase and others are governed by individual structural element which is called a cell.

4.2.1 Cell Structures

Both continuous and isolated structural elements filled with gas can be presented in polymer matrix. (See FIGURE 4.1) The differences between these two structures lead to different absorptions for moisture, different dielectric and heat insulation ability and different permeability.

![FIGURE 4.1]( Closed Cell and Open Cell [6])

For open cells dominated structures, the incorporated gas will eventually be dissipated along with time after processing. So, the gaseous phase inside the matrix is mainly air. However, since the membranes of closed cells prevent gaseous phase from escaping, the gaseous phase of closed cells dominated structures could be any incorporated gases like carbon dioxide and nitrogen. Although gaseous phase is soluble and diffusive, the existence of these introduced gases could influence properties of foams. What’s worse is that some specific gases possessing different diffusion rate causing internal pressures within cells. Inter pressures could damage foams as well as affect properties of foams.
4.2.2 Cell Density

Cell size and the number of cells are also concerned as major factors affecting foam properties. One of the reason is both of these two factors have great impacts on foam density. Density is one of the most significant parameter defines mechanical, thermal and electrical properties of foamed materials. Based on many studies, an increasing density indicates an increase in stiffness and yield strength [7,8]. Large cell size is directly corresponding to lower foam density [9]. Small cells usually mean a higher density with better energy absorption property and improvement on distribution of gaseous phase. On the other hand, regarding the number of cells, the estimated number of cells in 1 cm$^3$ isotropic polymer foam is from 1,000 to 10,000. The number of cells per unit volume is considers as a significant parameter describing nucleating agent behavior and consistency of foam structure.

4.2.3 Anisotropy

Anisotropy of cellular structure is cause by mechanical stresses generated in foaming since bubbles along the direction of foaming have more space and energy to expand. As a result, a cell stretching phenomenon occurs specially in low-density foams.

This anisotropy of cellular structure is going to change the properties of foam. Mechanical properties including strength and stiffness along foaming direction which the cell stretching occurred are much lower than properties along other directions [10]. In fact, there is more than one such direction in foam along different angles.

4.3 Foaming Agents

Foaming agent, which can be either a surfactant or a blowing agent, is a significant component or a facilitator during foam processing. The reason to used surfactant is that surfactant can reduces surface tension of gaseous bubbles to increase stability of formed cellular structures. Also, it is a cost-effective admixture comparing with others. Nevertheless, the performance of surfactants is not satisfied since most processing methods requiring a strong blowing power or large amount of gas formation inside the melt to expand the polymer into desired foams.

The blowing agents, which are usually gases, organic or inorganic liquids and solids, can be implemented into the melt to impart the blowing power or generate gases needed to force expansion. Two major categories of blowing agents that have been widely accepted are physical blowing agents (PBAs) and chemical blowing agents (CBAs). Some interesting parameters used to
Foaming

define Bas are the gas number, initial temperature and temperature range of decomposition, rate of gas liberation and internal pressure.

### 4.3.1 Physical Blowing Agent

Generally, physical blowing agents include low-boiling volatile liquids such as ethers, ketones, aromatics, and alcohols that can be transformed into gaseous state during abrupt change of temperature and pressure. Compressed gases or directly injected gases are also used as physical blowing agents. Some good examples of these gases are carbon dioxide and nitrogen. Air, which is considered to be an abundant and cheap material, is not applied as a PBA because of oxidizing effect of contained oxygen [11].

Like discussed in the beginning of this section, PBAs will impart a blowing power in the melt to expand the polymer. The intensity of blowing power is determined by vapor pressure of the gas. To reach an ideal foam density, the blowing power and volume of gases that PBA produced must be controlled. A prediction model (equation 4.1) that has been developed by Bheravesh, et al. is used to find this ideal expansion condition [12].

\[
\frac{V_{\text{polymer}} + V_{\text{gas}}}{V_{\text{polymer}}} = 1 + \frac{m_{\text{gas}} * v_{\text{gas}}}{m_{\text{polymer}} * v_{\text{polymer}}} 
\]  

(4.1)

Where, V, v and m are volume, specific volume and mass for gas and polymer, respectively.

Although such a relation was found to define the ideal expansion or ideal expansion ratio, perfect results have never been obtained in lab tests. Several reasons including gaseous bubbles escaping from polymer surface, partial gas remaining dissolved in the polymer and poor transport property of polymer due to high viscosity directly lead to the inefficient expansion. Gas diffusion, plasticization of the polymer and other factors should be controlled to guarantee an efficient expansion [13].

### 4.3.2 Chemical Blowing Agent

Chemical blowing agent is very different from physical blowing agent in terms of gas formation process. Comparing with physical blowing agents, chemical blowing agents will undergo a heat-induced decomposition which changes it from solid state to gaseous state. So, CBAs are compounds that liberate gas as result of chemical reactions like thermal decomposition of CBAs or interaction between CBAs and polymers. The ammonium salts of inorganic or organic acids and carbonates of alkaline are representative examples of chemical blowing agents. Advantages of using CBAs are: 1.
Easiness to process with most equipment; 2. Easiness to introduce them into the melt. Several requirements have been established by many researchers to choose a CBA and these requirements are summarized below [14].

- Decomposition temperature of CBAs should be close to melting point and hardening point of polymer
- Liberation of gas should be controlled within a narrow temperature range and the rate of liberation must be high
- Thermal conditions must be under control during processing to avoid negative effects on polymerization and foam structure
- Final products should be safe to use without concerns on toxicity, flammability, corrosiveness, etc.

Foams manufactured by using inorganic CBAs hardly can reach good quality because of poor dispersion within polymer matrix. Liberation rate of inorganic CBAs are also too high results in bad structural uniformity. Organic CBAs are not associated with this problem because the liberated gas is irreversible. The liberation rate can be maximized due to thorough mixing and temperature range that allows polymer to flow. However, organic CBAs are expensive with some specific toxic substances. Some of these blowing agents are also able to polymerize polymer matrix which leads to instable thermal conditions. Commonly used organic CBAs are azo and diazo compounds, N-Nitroso compounds, sulfonylhydrazides, esters and triazines [15]. Functional groups of listed compounds are exhibited in FIGURE 4.2.

![Functional Groups of commonly used CBAs](image)
4.4 Foaming Techniques

Foaming is a thermo-dynamic process which involves changes in relation among the product volume, surrounding pressure and temperature. Foaming techniques have been well developed to manufacture foam products of high quality. Several widely applied foaming techniques will be discussed in this section. Before introducing details of each processing method, key steps of foaming process are summarized in TABLE 4.1.

<table>
<thead>
<tr>
<th>Step</th>
<th>Implementation</th>
<th>Saturation</th>
<th>Liberation</th>
<th>Evacuation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>Introduce gas into polymer</td>
<td>Homogenize mixture</td>
<td>Liberate gas bubbles</td>
<td>Remove gas bubbles</td>
</tr>
<tr>
<td>Mechanism</td>
<td>Mixing/injection</td>
<td>Dissolution</td>
<td>Foaming</td>
<td>Permeation</td>
</tr>
</tbody>
</table>

4.4.1 Extrusion Foaming

Extrusion foaming is conducted by using an extruder which is an effective equipment to plasticize thermoplastics. It is important to have a difference between the melting point and the decomposition temperature of polymers to successfully manufacture foams. Having a large processing specific volume because of the design of extruder, efficiency of heat transfer for extrusion is guaranteed. Many other advantages like controllable internal pressure and short processing time are also reinforced by improvement of the design [16].

Extrusion foaming starts with plasticizing the polymer into a melt which is basically a state change of polymer due to applied heat. Extruder is designed to have a part that separating melted polymer and polymer in solid state to be energy effective. The following step is to introduce a gaseous phase into the melt. Solubility and diffusivity play significant roles in the dissolution stage. Sorption, defined as the amount of gas incorporated into the melt, is closely related to the unit mass of gas and its vapor pressure [17]. Since foaming and solubility of some gaseous blowing agents are both pressure and temperature controlled, it is critical to have a system in the equipment to adjust the conditions. Another study emphasized the importance of transport capability of gas in polymer melts. The state of polymer and morphologies of polymer chains more or less determines if the gas is able to transport through the melt to have desired expansion or dispersion of bubbles. After continuing rotation and heat application, it is expected to have a homogeneous mixture that will undergo cooling. Once the mixture is stable, it will be pumped to begin foaming process. Key
element of an extruder is its screw because it is the “source” of mechanical energy and heat. Single screw, twin screw and multi-screw are normally adopted. No matter which kind of screw has been used, the length to diameter ratio decides its ability to process polymers [18].

In early 1950s, foaming of polystyrene and polyolefin were developed by using extrusion technique and many polymers can be processed now. Also, the dimensional limit has been solved by using post-foaming shaping equipment. Sheets, slabs and rods are now available by foaming in an extruder.

4.4.2 Thermoset Reactive Foaming

Thermoset reactive foaming is a foaming process based on chemical reactions leading to liberation. It is designed to take the advantages of thermosets with interesting properties. Epoxy, polyurethane and phenolic can be expanded to suggested geometry by using reactants.

Different processing methods of reactive foaming have different advantages and disadvantages. Continuous processing method enables maximum expansion at a high speed. However, the expansion is not uniform and the cooling period is long. Semi-continuous processing method has a relatively high yield, but, its processing efficiency is questioned. The last method is batch processing method providing a restrained foaming inside a mold. In other words, its expansion is limited and the requirement of mold design is high. Difference should be noticed between reactive foaming of thermoset and thermoplastics. For CBAs applied in thermoplastic foaming, a heat-induce decomposition occurs within polymer matrix.

A good example of reactive foaming is polyurethane foams. This type of foams is often made through chemical reaction between isocyanate like TDI and polyol. A catalyst is required as well as other additives to increase reactivity and control reaction temperature. Either free expansion processing or constrained expansion processing can be applied for PU foams.

4.4.3 Injection Molding Foaming

Injection molding is welcomed in foaming industry due to the variable design of mold and rams tonnage. Reactive injection mold foaming, co-injection structural mold foaming and microcellar injection mold foaming are three commonly accepted processing methods. Reactive injection mold foaming is to pump chemicals in liquid state to mix with polymer then start foaming in the mold. (See FIGURE 4.3) Despite of fundamental aspects, injection molding foaming is very different from extrusion foaming in terms of limit of expansion. Comparing with free expansion of extrusion, expansion of mixture inside mold for injection molding foaming is
restrained. In recent years, co-injection mold foaming and micocellar injection mold foaming are well developed and applied in injection molding. Co-injection mold foaming is to inject two polymers or same polymer at different foaming degree into the mold to more compact structure. Microcellar injection molding is to generate a cellular structure with tiny cell size by using a physical blowing agent. The yield of such a method is relatively high and the processing time is short.

Overall, injection molding foaming is a better technique in terms of foaming control since it has controlled expansion comparing with extrusion. Smaller cell size and higher density are more likely to be achieved by using injection molding foaming to ensure good performance of foams.

4.4.4 Molded Bead Foaming
Molded bead is another well-developed technique in foaming industry. The molded bead foaming uses a physical blowing agent to absorb resins into a super-saturation state at a high temperature or a low pressure. Accelerator which is often a liquid state medium is needed to enhance saturation. Initially, beads are in a free form or under a constrained expansion. Controlled expansion will make cell size really small to improve insulation and mechanical properties. One concern related to molded bead foaming is discontinuous processing due to the batch nature which results in low processing efficiency. Many efforts have been made to the foaming of polyolefin and it is founded that x-linked polyethylene can be foamed into mold bead products with finer cells and better structural stability [20].
4.4 Applications of Foams

Consumption of polymeric foams is increasing over the years with many more new foamed materials developed. Rigid or flexible polyurethane foam is one of the earliest foam that has been widely used and it has still been using due to its variable densities and cell structures. Packaging materials, seats of automobiles, liners, furniture, recreation items, and appliance can all be made of flexible or rigid PU foams. Polystyrene foams are another commonly used foam materials. PS foams are selected to use due to its great insulation capability, low density and rigid structure [21]. The most common products of PS foams are PS foam sheets and PS foam slabs. PS foam sheets are mainly used in food industry and PS foam slabs are mainly used as insulation materials in construction or packaging materials. With same density, rigidity of PS foam is higher than rigidity of other foams. Conductivity of various foams is also relevant to density. (See TABLE 4.2)

<table>
<thead>
<tr>
<th>Types of Foams</th>
<th>Density, kg/m³</th>
<th>Conductivity, W/(m*K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS Foam</td>
<td>24</td>
<td>0.029</td>
</tr>
<tr>
<td>PE Foam</td>
<td>35</td>
<td>0.051</td>
</tr>
<tr>
<td>PU Foam</td>
<td>24</td>
<td>0.023</td>
</tr>
<tr>
<td>PET Foam</td>
<td>140</td>
<td>0.014</td>
</tr>
<tr>
<td>X-PE Foam</td>
<td>30</td>
<td>0.036</td>
</tr>
</tbody>
</table>

The mostly consumed polymer is actually polyolefin which is a major supporter of today’s foaming industry. Beginning in 1970s, along with the development of molded bead foaming technique, PE and PP foams became popular to use to make packaging materials, automobile seats and recreation applications. In comparison with PS foams which are also largely used to make products mentioned above, PE foams possess a better chemical resistance and resilience [22]. These advantages were found and applied in manufacturing of life jackets and surfing boards.

Other foams are also developed to use in different industrial areas. PET foams, PVC foams and epoxy foams are usually encountered in our daily life. PET foams are famous for barrier properties meaning good thermal and dielectric insulation. PVC foams are mostly being used for their moderate strength, good insulation and, most importantly, the polar nature which improves adhesion to commonly seen coating materials. Epoxy foams have excellent dielectric insulating abilities. So, they are widely used to make electronics or electrical components.
References


5

Devolatilization

by Andrew Cascione

5.1 Background

Prior to processing, polymer melts often times contain residual volatile components such as unreacted monomers, solvents, precipitators (e.g. water) or non-polymerizable compounds. These volatiles originate from raw materials used for various polymerization techniques and from reaction by-products. Separating and removing them from the polymer matrix is referred to as devolatilization [1]. It is a fundamental step in polymer manufacturing as impurities can adversely affect polymer properties. End-market specifications require polymers to possess certain physical properties which dictate the removal of solvents to low levels. Residual monomers must also be removed, particularly during step-growth polymerization, as their presence can limit polymer molecular weight [2]. Some monomers also emit strong, offensive odors that can be problematic for food packing products.

Unreacted monomers may also need to be eliminated for environmental and occupational safety reasons. Polyvinyl chloride (PVC) plants, for example, can be particularly dangerous due to the serious health hazards associated with vinyl chloride monomer. Raw materials used to make commodity polymers can also be toxic and/or flammable, as in benzene, which is used to synthesize polystyrene.

Many solvents and monomers are categorized as volatile organic compounds (VOCs). Strict environmental regulations require low emission levels of VOCs. The Clean Air Act of 1990 designated 189 substances as hazardous air pollutants (HAPs) which are regulated by the Environmental Protection Agency (EPA). Many monomers and solvents used in polymerization are listed as HAPs. Economics rather than regulations, however, may be a larger concern for manufacturers. In the case of solution and slurry polymerization techniques, solvents are used as the medium to carry out the polymerization reaction. The costs of these solvents incentivize
manufacturers to recover them as well as other materials captured from plant waste streams [3].

In industrial settings, devolatilization equipment is attached downstream from the reactor. After leaving the reactor, the polymer is pumped in a molten state above the glass transition temperature to one or more pieces of devolatilization equipment which expose the polymer melt to vacuum conditions. Vacuum driving forces separate the solvents and remaining monomers from the melt by reducing the ambient pressure below the equilibrium partial pressure of the volatiles. A diffusion driven, mass transfer phenomenon then transports aqueous low-molecular-weight components to a liquid-vapor interface where they are converted from the aqueous phase to the vapor phase for subsequent removal and collection. In bulk and suspension polymerization techniques, pressures are low enough to induce foaming in the polymeric system which reduces the distance volatiles must diffuse to a liquid-vapor interface. The processes may be aided by adding a stripping agent such as steam or nitrogen which assists in bubble creation and lowering the partial pressure of the volatile in the vapor phase. The ultimate goal of this operation is to reduce volatiles below 50-100 parts per million (ppm) [4].

5.2 Historical Developments

Many polymers undergo an initial flash during the devolatilization process where a large percentage of volatiles will separate from the melt by rapidly boiling off. The remaining polymer solution will typically still contain a small amount of volatiles (less than one percent) that need to be removed. The best methods to remove small amounts of volatiles from highly concentrated polymer solutions and how to model that process was a topic of research starting in the 1960’s (see reference 1). Since the devolatilization finishing process was often done using rotary equipment such as a vented extruder, the research focused on devolatilization during the extrusion process.

In 1970, Roberts authored a paper expounding upon the conventional wisdom at the time which advocated a surface renewal model to explain devolatilization during extrusion under vacuum pressures [5]. In the surface renewal model, devolatilization of polymers with low levels of volatiles using rotary equipment was said to be governed solely by volatiles diffusing at the surface of the pool by a bubble free mass transfer. It was concluded that concentration gradients existed only at the surface where the volatile components diffuse through the aqueous-vapor interface to the vapor phase.
Devolatilization was made possible during extrusion since the surface of the polymer melt was continually renewed by rotating flights in the screw.

Biesenberger and Kessidis (1982) later discovered that devolatilization of polymers with very low levels of volatiles during extrusion under a vacuum was not just a simple molecular diffusion process, but dependent on vapor bubble nucleation, growth, and transport which speeds up the mass transfer process [6]. They evaluated the devolatilization efficiency of a polymer melt in the single-screw extruder under pressure, with and without nitrogen. Nitrogen was used since it prevents the release of volatiles through bubbles. In this experiment, the devolatilization efficiency was found to be greater without nitrogen. They subsequently concluded that bubbles do nucleate and assist devolatilization during extrusion, even at polymer concentrations with less than 50 ppm. Since then, bubble transport models have been developed for extruders and other types of equipment.

In 1990, Albalak et al., published a seminal paper confirming earlier research. They conducted a systematic study of bubble morphology using scanning electron microscopy [7]. Prior to this study, it was assumed bubbles occur suddenly and uniformly in a polymer melt. Their research showed that devolatilization proceeds through a blistering mechanism where minute blisters first form which become nucleation sites for microbubbles that grow and coalesce into macrobubbles.

5.3 Thermodynamic Fundamentals

Devolatilization is a separation process and therefore thermodynamically driven. Understanding the thermodynamics of polymer solution equilibrium is necessary for determining the amount of volatiles that can be separated under a given set of processing conditions. The total pressure within a vacuum chamber needs to be lower than the partial vapor pressure of the volatile in solution with the polymer, $P_1$, for the volatile to vaporize. This devolatilization process is a mass transfer operation that continues until the weight fraction of the solute in the polymer, $W_e$, is at thermodynamic equilibrium. The arranged Flory-Huggins equation in (1) allows for the calculation of the $W_e$, when the vapor pressure of the pure volatile component, $P_1^0$, the density of the pure volatile, $\rho_1$, the density of the polymer, $\rho_2$, and the dimensionless Flory-Huggins solubility parameter, $\chi$, are known, all at a specific temperature (see Reference 1).

$$W_e = \frac{P_1 \rho_1}{P_1^0 \rho_2} e^{-(1+\chi_{12})}$$  \hspace{1cm} (1)
The practical application of this relationship allows for the calculation of the desired combination of pressure and temperature needed to vaporize a solvent from a polymer. As $P_1$ is lowered, the volatiles separate from the solution which forces $W_e$ to equilibrium conditions. Ideally, the desired $W_e$ would always be reached with the set $P_1$. However, reaching thermodynamic equilibrium is challenging in industrial settings due to equipment imperfections and economic constraints that require devolatilization processes to only last for limited times.

To help drive the system toward equilibrium, free volume concepts can be taken into consideration. As the temperature of polymer is increased, the kinetic energy of the polymer chains increases. This leads to an expansion of the material at a molecular level which increases room for volatiles to diffuse through the polymer melt. Consequently, an increase in temperature enhances the rate of diffusion in a polymer-volatile system. While thermodynamics dictate that a low vapor pressure at the surface of the polymer melt is needed to create a concentration gradient to drive the diffusion process, an increase in temperature increases the diffusion rate. Therefore, many devolatilization systems operate at the highest temperature possible to reduce the viscosity and enhance the diffusion process.

Too high of a temperature during devolatilization, however, can significantly degrade or damage the polymer. This is especially true during the ending stages of devolatilization as polymer viscosity increases due to a reduction of volatiles. As the viscosity increases, high temperatures are needed to keep the polymer workable. Additionally, some polymers have a polymerization ceiling temperature where they can depolymerize. This is known as “unzipping” a polymer [8]. If the temperature is high enough, the bonds of a polymer chain will break and monomer will be thrown off. This is essentially the reverse of the polymerization step. Since the monomer fragments have a lower equilibrium vapor pressure, they will begin to vaporize resulting in disastrous production consequences. This phenomenon is especially relevant during the production of poly(methyl methacrylate) which has a low ceiling temperature. To avoid thermal damage or depolymerization, pressure-temperature operating “windows” are determined for specific polymer-volatile solvent systems.

5.4 Bubble Nucleation and Growth

Diffusion coefficients of monomers and other volatiles in concentrated polymer solutions are very low ($10^{-14}$ to $10^{-18}$ m$^2$/s) potentially causing devolatilization to be a very slow process [9]. These coefficients determine the time takes for a volatile to migrate to the surface of a pool melt. The
devolatilization rate can be increased by generating bubbles of volatile gases that increase the area available for mass transfer from the polymer to the vapor phase. Hence, the growth of bubbles containing vapor of the volatile material is recognized as a crucial stage in the devolatilization process.

In order for bubbles to nucleate, the polymer melt must be superheated. Superheated conditions occur when the temperature is raised above the value at which the equilibrium vapor pressure equals the surrounding pressure over the polymer melt, or when the pressure is reduced below the vapor pressure. Under superheated conditions, the polymer melt is metastable and will only reach equilibrium when it breaks up into two phases.

Volatile vaporization through bubble transport mechanisms can be distinguished into three separate regimes [10]. The first regime is described as “free-boiling”. This occurs when the total pressure in the vacuum chamber is less than the partial equilibrium pressure of the volatile as described in 5.3. It occurs in volatile rich polymer solutions. During free-boiling, vapor bubbles rapidly nucleate, expand, and rupture. This results in a rapid decrease in temperature. For example, a styrene-polystyrene melt at 250°C will drop approximately 12°C for every 10 percent reduction of the volatiles by weight of the solution to vaporize. A reduction in temperature leads to a drop in the partial equilibrium pressure of the volatile which diminishes the amount of superheat. The free boiling regime phases out as the bubble growth slows down and the polymer melt transitions into the second regime termed “bubble growth”.

In the bubble growth regime, the superheat decreases and the viscosity increases due to a reduction in volatiles. As a result, bubble initiation is limited and the temperature begins to equilibrate.

In the third regime, the viscosity of the polymer melt is very high, the degree of superheat is very low, very few bubbles are formed, and the rate of volatile loss is very slow. In this environment, diffusion becomes the rate determining step. The polymer melt is under the same conditions as discussed in 5.2 where the remaining polymer solution contains a small amount of volatiles. Under these circumstances, devolatilizers with rotating machinery are preferred to generate new surfaces in the pool melt and induce shear stresses.

Bubble growth and rupture can be enhanced by shear flow in the polymer melt [11]. Shear stresses aid in the quick detachment of pre-existing bubbles which multiplies the number of bubble nucleation sites. Shear stresses also deform bubbles which creates more service area for the transfer of volatiles from the polymer melt to bubbles. Therefore rotary devolatilization equipment is designed to maximum bubble disruption.
5.5 Commercial Equipment

A wide variety of devolatilizing technologies currently exist. To decide which type of technology to use, one must consider the residual monomer concentration of the polymer melt, investment costs, space requirements, energy consumption, and overall efficiency. The viscosity of a polymer melt is a significant issue as well, since higher viscosities limit mass and heat transfer as well as affect bubble formation. To devolatilize high viscosity melts to low monomer levels, it’s necessary to generate enough heat, surface area, and vacuum. The melt also has to be properly distributed and/or mixed in the devolatilizer to prevent overheating or hotspots.

Devolatilizers can be classified into two main categories: static and rotating equipment. The most popular types of static devolatilizers are flash evaporators and falling-strand evaporators. In static devolatilization, there are no moving parts. Volatiles are removed by evaporation from a falling strand (film) of a polymer melt. The advantage to this type of technology is less installation and maintenance costs, reduced energy consumption, and no product degradation due to low residence time. Since polymer melts entering static machinery are volatilie rich, they often have low solution viscosities. Thus mass and heat transfer and surface renewal is typically not an issue [12].

Rotating devolatilizing equipment is better equipped to handle high viscosity polymer melts (> 10,000 Pa) since this type of machinery contains moving elements that transport the polymer melt within the devolatizer and impart surface renewal for heat and mass transfer. Shear forces enacted upon the polymer melt help generate bubble nucleation [13]. However, this requires rotating equipment that possess complex designs and have large energy requirements. The most widespread devolatilizers of this type include single-screw and twin-screw extruders.

5.5.1 Flash Evaporators

Flash evaporators consist of a heat exchanger and a flash chamber. The polymer solution is first pumped to a heat exchanger where it is heated up and pressurized to decrease its viscosity for efficient discharge. It is then pumped into the top of the flash chamber where the pressure is relieved and boiling occurs. The pressure maintained in the flash chamber is low enough so it is below the saturation pressure of the volatiles in the melt. As the solution falls through the flash chamber, a multitude of bubbles is nucleated in the solution. This results in a large amount of surface area for mass transfer of the volatiles from the aqueous phase to the vapor phase leading to a rapid devolatilization of the polymer. The vapors are collected and
pumped to a condenser. Meanwhile, the residual polymer collects at the bottom of the chamber and is pumped away. A back pressure valve in between the heat exchanger and flash chamber is used prevent premature boiling in the heat exchanger [14].

In a single step of flash evaporation, a solution of about 15% polymer will increase to as high as 95% polymer. However, the first flash typically does not remove all the volatiles necessary to meet market demands and a second flash is needed. At this point, since polymer has a higher viscosity and does not contain as much volatiles, it will not foam as will on its own. Therefore, prior to the second flash evaporating stage, a stripping agent is added to further reduce the partial pressure of the volatile in the vapor phase and improve melt foaming. A second preheater may also be necessary. After one or more flashes, the polymer can be pumped to a finishing unit such as an extruder. This process is known as staged devolatilization and has been effective in reducing volatile concentrations down to 50 ppm. Polymers successfully used for this process include polystyrene, polycarbonate, acrylics, and elastomers [15].

5.5.2 Falling-Strand Devolatilization

As the polymer falls through the flash chamber, even distribution is needed for optimal flash efficiency. Some flash chambers have specially designed nozzles for which spray the polymer into the chamber as falling strands. These types of flash evaporators are called falling-strand devolatilizers and operate similarly to flash evaporators [16].

The conditions in a falling-strand chamber and designed to promote bubble growth and increase the diffusion process. Before pooling at the bottom of the chamber, the melt may first fall on a conical, birthday hat shaped device to prolong exposure time in the chamber vacuum.

5.5.3 Screw Extruders

Polymer devolatilization commonly takes place during the extrusion processing technique. “Vented extruders are the most frequently used rotating-type devolatilizers” (see Reference 1). This is because they have several combinations of features that make them so useful. They can effectively pump a highly viscous polymer melt, generate heat as a result of mechanical work on the melt, and provide enough volume for the melt to foam. There are two basic types of extruders, a single-screw extruder and a twin-screw extruder.

In an extruder system, feed polymer is delivered into a hopper which drops the feed onto a rotating screw containing flights that move the polymer along the surface of the screw. As the polymer feed moves through
the extruder, it is melted, pressurized, and forced out a die opening, taking the shape of the die. To devitalize the polymer melt, vent ports are added along the extruder so gasses and moisture vapors may escape. The vent port design in extruders where volatiles travel with the polymer up to the vent port is referred to as forward vents. The length of the vent zone can be between 2 and 5 times the screw diameter. The vent zone of the screw contains deep channels that allow the polymer to be exposed to low pressures (vacuum) and to accommodate foaming. In order for the volatiles to escape from the polymer melt, there can be no positive pressure in the vent port section of the extruder. In this section, screw channels are partially filled so the free surface area of the melt pool is continually renewed to optimize the degassing process. This is known as starve-feeding the extruder [17].

In some processing applications, it may be desirable to place the extruder next to the polymerization reactor so extrusion in conjunction with devolatilization can be used as a processing finishing step. In this case, the extruder is melt-fed and can have a rear vent design as opposed to a forward vent design. In the rear vent design, volatiles are extracted upstream of the feed opening.

Many models postulate the mass transfer rate of volatile components through the polymer melt is dominated by molecular diffusion at the surface of the pool melt [18]. These models calculate the amount of volatiles that will be “devolatilized” by factoring the life span of each newly created surface layer. Therefore, the geometry of the flights on the screw, screw speed, and feed rate are optimized so the melt surface is frequently renewed. These models have limitations, however, when bubbles are generated inside the melt pool (foaming). During foaming, volatiles also diffuse from the melt into the bubbles where they grow, transport to the surface, and rupture. Since bubble transport substantially improves the separation efficiency, foaming or “stripping agents” such as water are often added to the polymer to enhance bubble nucleation. Shear forces induced by the rotating flights also promote bubble nucleation. Foaming is a relatively quick phenomenon during extrusion. A study conducted by Tukachinsky et al. (1994), recorded the strongest amount of foaming in an extruder rotating at 72 rpm occurring during the first 5 seconds and terminating at 30 seconds [19]. More intensive foaming occurred with higher screw speeds.

5.6 Industrial Applications

The challenges of volatile and monomer removal are different for polymerization techniques used during production. Therefore, different
devolatilization methods are recommended based on the polymerization technique utilized. Polymerization techniques can be divided into several categories: bulk polymerization, solution polymerization, gas-phase polymerization, slurry polymerization, and suspension polymerization.

In bulk polymerization, the only the monomer and the catalyst or initiator are the components used for the process. Examples of bulk polymerization produced by free radical polymerization include low density polyethylene, polystyrene, poly(methyl methacrylate), and those produce by step-growth polymerization include poly(ethylene terephthalate), polycarbonate, and nylons. After free radical polymerization, devolatilization is necessary to remove and recover excess monomer. During step-growth polymerization, devolatilization is conducted as the driving force to enhance the polymerization reaction. In either process, bulk polymerization often results in high viscosity melts which can be challenging to handle. Temperature increases can reduce viscosity, but care must be taken not to thermal degrade or unzip the polymer.

A popular remedy to this situation is to added an organic solvent and polymerize the monomer in solution [20]. On one hand, a solvent will reduce heat generation and lower the viscosity. On the other hand, low polymer concentration results in a multistep devolatilization process. One or two flash devolatilization steps followed by a vacuum extrusion have proven to be effective approaches.

For the production of polyolefins such as polypropylene and high density polyethylene, free radical polymerization is conducted at high pressures (10,000 to 50,000 psi) in slurry processes using up to 90 percent solvent. In this scenario, residual monomer and solvents can be removed from the solution by transferring the polymer melt from the reactor to a vessel with a lower pressure. This process must be carefully controlled to prevent an explosion from occurring (see reference 1).

During emulsion polymerization, polymers are produced by an aqueous dispersion process, most often using water. Styrene-butadiene rubber and latexes are produced using this method. Both post-polymerization and devolatilization process are used to reduce the residual monomer. Post-polymerization is conducted when initiators are added at the end of the polymerization process to create new polymers. In devolatilization, the polymer (latex) is stripped using steam or gas under vacuum conditions [21]. Large amounts of foaming in this process are undesirable as it can cause coagulation.
5.7 Concluding Remarks

Scientific research of the devolatilization process has made significant gains in the past 40 years. Accurate understanding of devolatilization mechanisms and subsequent modeling and will help plant manufacturers design devolatilization equipment parts and improve plant “scale-up” efficiencies. Continued research in polymer devolatilization is needed to improve upon the exact temperatures, pressures, and operating conditions needed for optimal devolatilization processes.

The literature reviewed indicates that solvents will be continued to be used for future polymerization processes. Therefore, devolatilization will continued to be a fundamental step of polymer production in the foreseeable future to confine/recover the solvents. Strict environmental standards as well as polymer demand for technologically advanced applications will dictate their reduction in the final product.

References

Blown Film Extrusion, also called Film Blowing, is one of the important polymer processing methods. This is a process by which most commodity and specialized plastic films are produced. They have applications in
numerous areas, but most widely in commodity applications, such as packaging and bags.

### 6.1 Introduction of Blown Film Extrusion

The film blowing process basically consists of extruding a tube of molten thermoplastic and continuously inflating it to several times its initial diameter, to form a thin tubular product that can be used directly, or can be used as flat film after being slit.

Blown film extrusion has several advantages over flat-die, cast-on-carrier extrusion, or other typical methods used to manufacture film and sheet. It has:

1. **Ease to control:**
   - Produce tubing in a single operation;
   - Change the film width and thickness by control of the volume of air in the bubble, the output of the extruder and the speed of the haul-off

2. **Better performance:**
   - Eliminate end effects such as edge bead trim;
   - Capability of biaxial orientation, allowing uniformity of mechanical properties;
   - Permits the combination of a number of different materials to obtain various properties;

3. **High productivity**
   - One die can make many different widths and sizes without significant trimming. This high level of flexibility in the process leads to less scrap material and higher productivity.

But there are also some disadvantages:

1. Less effective cooling process than flat film. Flat film cooling system because it is done by means of chill rolls or water, which is better than air.
2. Compared to cast film, blown film has a more complicated and less accurate method to control film thickness.
3. The melt flow index for cast film is about 5.0 g/10 min whereas for blown film it is about 1.0 g/10 min. The production rates for cast film are higher: cast film lines can reach production rates of up to 300m/min whereas blown film lines are usually less than half this value.
4. Cast film has better optical properties.
Despite the disadvantages, the film blowing processing is one of the most important processing methods. And even the vast majority of polymer films are manufactured by this method.

6.1 Materials for Processing

Various materials can be extruded by this process to make blown film. Polymers and additives are two broad categories of materials that are used in the process. Lots of different polymers can be used, such as polyethylene and polyurethane. However, various grades of polyethylene occupy the vast majority of the polymers. Additives are also added for certain purpose, such as to have a certain performance, appearance or in the consideration of economic issues. Here, in the next sections, discussion will be focused in different polymer used for film blowing.

The material to be used for the process is usually determined by the desired property for different applications. As to the final product properties, processing properties are also very important in material selection. Ease of processing in blown film can be described by characteristics such as good thermal stability, high melt strength (outside of the die), reasonable head pressures, and no melt fracture, which means film surface imperfections. Finally, minimal cost is also a key factor that needs to be taken into consideration.

As talked above, blown film is mostly used for commodity applications, such as packaging. Polyethylene is an ideal polymer for most applications. Within the broad family of polyethylene, there are several types that find application in blown film. There are, however, other polymers used as well. The following sections detail the many polymer types used in blown film extrusion.

6.1.1 Polyethylene (PE)

Polyethylene (PE) is the simplest polymer from a chemical standpoint. PE is polymerized from ethylene monomer and consists of a carbon chain backbone with two hydrogen atoms bonded to each carbon atom (shown in figure 6.1). PE chains could be very linear or branched due to the way how the polymer was synthesized. PE is lightweight, water-resistant, has a good balance of strength and flexibility, and can provide some clarity. Besides, PE is easy to extrude and heat-seal and, most importantly, is of low cost. Furthermore, PE is a polymer well studied scientifically, which means designing and controlling specific properties are possible.

Blown film processing methods for PE can vary depending on the grade. However, one important similarity is that all PE grades have a high value of
specific heat, which means that heat removal from the melt is relatively slow. It takes time to remove enough heat from the two layers passing through the nip rollers to prevent them from sticking together and that is why cooling towers for PE processing are usually very tall.

Figure 6.1 A short section of a polyethylene molecule

Polyethylene is often categorized by its density, a measure of the mass per unit volume. There are Low-Density PE, High-Density PE, Linear Low-Density PE and Metallocene PE.

I. Low-Density Polyethylene (LDPE)

Low-density polyethylene consists of short chain branches and long chain branches, which prevent crystallization. The low level of crystallinity results in lower density. LDPE is relatively easy to process for it melts at a relatively low temperature and does not require much extruder motor power. LDPE blown film grades are moderately high in viscosity, but the wide range of branching yields a wide processing window and high melt-strength in the bubble. This leads to a stable bubble. Besides, LDPE heat-seals very easily.

LDPE blown film are tough and flexible. The toughness is due to the good combination of strength and elongation, particularly when processed with high machine and transverse direction orientation. Low crystal content gives the polymer good flexibility. Thus, LDPE bags provide a soft feel compared to the HDPE bags. But, as expected, LDPE is not as stiff or strong as HDPE.

II. High-Density Polyethylene (HDPE)

High-density polyethylene is synthesized by a method that very linear chains can be produced which results in a high percentage of crystallinity. Processing HDPE is different from processing LDPE. HDPE melts at a higher temperature (130 to 135 °C) and has a narrower processing window. It also requires higher screw torque, hence more motor power. HDPE has lower melt strength, so to delay of transverse stretching of the bubble is needs until the melt is cooled. Thus, the bubble remains more stable.

HDPE has high strength and stiffness among polyethylene grades. As a result, there is continual progress in the area of reducing the thickness of HDPE film products. Additionally, HDPE has reasonably good barrier properties owing to its high degree crystallinity.
III. Linear Low-Density Polyethylene (LLDPE)

Linear low-density polyethylene (LLDPE) is synthesized similarly with HDPE, but LLDPE has a much higher content of co-monomer. By controlling the amount of branch points through co-monomer content, degree of crystallinity and density can be altered.

With regard to processing, LLDPE is something of a mixed bag. Inside the extruder it performs similarly to HDPE, requiring higher torque and often employing a grooved feed throat. However, outside of the die it is generally processed with a pocket bubble like LDPE, even though the melt strength tends to be lower than that of LDPE. As to the LLDPE solid-state, the strength is higher than that of LDPE, approaching that of HDPE. However, it has the softer feel and lower stiffness of LDPE.

IV. Metallocene Polyethylene (mPE)

Metallocene polyethylene is a broad class of polymers made from ethylene that are synthesized using metallocene catalysts during the polymerization process. One of the key property benefits of mPE is the ability to synthesize very soft, flexible grades.

6.1.2 Polyurethane (PU)

Polyurethane is a highly versatile material with a wide range of properties. Its applications depend on the chemistry of the specific grade. Blown film grades are thermoplastic and either aromatic or aliphatic. Aliphatics are comparatively expensive, but generally have better resistance to ultraviolet radiation and are clearer. There are also polyether-based and polyester-based PUs. The former has better low temperature flexibility and the latter tends to be tougher and has better chemical resistance.

Blown film grades of PU are usually easy to process and have good melt strength. However, they are highly moisture absorbent and need complete drying before blowing processing.

Because of their high elasticity and toughness, PU blown films are generally used in specialty applications. One example is an adhesive laminating layer between fabrics.

6.1.3 Other Polymer

I. Polypropylene (PP)

PP is a kind of polymer that is able to crystallize. But, PP crystal structure is different from PE crystal structure and has a higher melting point. PP can be used in applications requiring a higher use temperature and more strength. Additional property sets are available from PE/PP copolymers, materials synthesized using both ethylene and propylene monomers.
Processing PP is similar in ease to processing PE without requiring drying and decrease in viscosity. But the lower melt strength of PP leads to difficulties with bubble stability.

II. Polystyrene (PS)
PS is a kind of amorphous polymers, and thus it possesses excellent clarity. High strength and low cost are two important commercial properties of PS. But PS is very brittle and PS films can crack easily when folded and slight imperfections. Thus, PS is generally blended with some amount of rubber-containing modifier. Blown film processing of PS is significantly more difficult than PE. Applications for single and multilayer PS films include food and candy packaging, clear gift wrap, and envelope windows.

III. Vinyl Acetate (EVA)
Ethylene vinyl acetate is a copolymer of polyethylene. It is similar in chemistry to PE. VA adds polarity or adhesion to the polymer and improves the compatibility of the polymer with. Most blown film applications using EVA food and electronics packaging.

IV. Ethylene Vinyl Alcohol (EVOH)
Ethylene vinyl alcohol is a copolymer of polyethylene with some percentage of the vinyl co-monomer along the chain. EVOH has some important commercial properties, the most important ones of which is its resistance to oxygen permeation and its water-solubility. Hence, it is used as a barrier layer in multilayer food-grade films and the delivery of laundry detergent via dissolving packaging.

V. Polyvinyl Chloride (PVC)
Polyvinyl chloride (PVC) is one of the most extruded polymers. PVC has limited thermal stability, but it has good melt strength. PVC is an amorphous polymer. As a result, it has good clarity. By adding a plasticizer to the polymer, it can be modified into either a rigid material or a flexible one. PVC has two other special properties, which are barrier properties and heat-shrinkability.

VI. Polyamide (PA)
Blown film polyamide is primarily used for barrier layers in multilayer structures. However, PA has quite different processing characteristics. PA has a much higher processing temperature, and PA absorbs moisture from the air, so it must be dried sufficiently prior to processing.

6.1.4 Additives
Practically, polymers are extruded with adding at least one type of additive. Additives represent a primary method to modify plastics
properties, such as strength, clarity, and cost. Additives can also improve the ability of polymer to be processed.

As to blown film process, additives may affect the processing of plastics in various ways. For example, some additives are designed to aid processing by reducing viscosity while others may have a detrimental effect on extrusion machinery by causing considerable wear.

Common additives for this processing method include:

- Anti-blocking Agents
- Antioxidants
- Antistatic Agents
- Colorants
- Lubricants
- Reinforcements and Fillers
- Stabilizers
- Tackifiers

6.2 The Processing and the Hardware

6.2.1 Processing

Blown film extrusion consists of two steps: the first step is regular polymer extrusion process and the next step is the film blowing process.

![Schematic of a Basic Blown Film Line](image)

**FIGURE 6.2** Schematic of a Basic Blown Film Line

The resin pellets are fed into the extruder through the hopper to obtain polymer. Then the plastic melt is extruded through an annular slit die, usually vertically, to form a thin walled tube. Air is introduced via a hole in the center of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of
film then continues upwards, continually cooling, until it passes through nip rolls where the tube is flattened to form a lay-flat tube of film. This lay-flat or collapsed tube is then taken back down the extrusion tower via more rollers. On higher output lines, the air inside the bubble is also exchanged. The lay-flat film is then either kept as such or the edges of the lay-flat are slit off to produce two flat film sheets and wound up onto reels. If kept as lay-flat, the tube of film is made into bags by sealing across the width of film and cutting or just applying perforating. This is complete in the blown film process line.

6.2.2 Hardware for Blown Film Extrusion

The hardware for Blown Film Extrusion mostly include four parts, which are

- Upstream Components
- Grooved Feed Throat
- Screws for Blown Film Extrusion
- Blown Film Dies

They are briefly discussed below.

I. Upstream Components: The Crammer Feeder

Pellets and fluff are the two most common forms of polymer form for blown film. When film is prepared for feeding into an extruder simply by grinding instead of re-melting/pelletizing, the resulting feed is a very low bulk density product known as fluff. But this form of polymer does not feed readily into an extruder hopper simply by gravity. Therefore, a Crammer Feeder is needed for feeding, generally some ratio of fluff with pellets

![Crammer Feeder](figure6.3)

FIGURE 6.3 A crammer feeder

II. Grooved Feed Throat
In many extrusion operations, the internal surface of the feed throat is smooth; however, for blown film, a grooved feed throat is more. The purpose of the grooved feed throat is to increase throughput.

The grooves act to increase the friction between the fluff and the barrel, allowing the screw flight to force more fluff forward with each revolution of the screw. The forward movement of the solid bed may approach piston-like efficiency. This will lead to an increase in the rate of melt flow through the die, which means a higher productivity.

III. Screws for Blown Film Extrusion

Because blown film extruders often utilize a grooved feed throat, the conveyance rate of fluff is generally very high. As a result, blown film extruder screws are typically designed for high viscosity melts. Deep flighted screws of conventional design (simple conveying screws) are susceptible to unmelt, a condition where particles that are not completely melted reach the end of the screw.

Many blown film screws today include a barrier flight. This second flight in the melting section of the screw helps to ensure that no un-melted material exits from the barrel. Because blown film products are very thin, unmelts can be quite problematic, both structurally and aesthetically.

IV. Blown Film Dies

The purpose of the blown film die is to receive polymer melt from the extruder and deliver it to the die exit as a thin annular (tubular) film. The most common type of die for blown film is the spiral mandrel die. Their laminar flow behavior mainly keeps the polymers in separate layers through the final product.
VII. **Other hardware**

There are also some other hardware in the processing line.

- An air ring, which blows air outside or inside the bubble and cool it.
- A bubble stabilizing cage, to stabilize the bubble.
- Nip rollers and collapsing frame, to pre-flatten the bubble.
- Winders.

### 6.3 Simple Dynamics

The specific shape of the bubble depends on the combined influence of several process parameters.

- **Die diameter** - die diameter represents the initial bubble diameter as it leaves the die,
- **Die gap** - the die gap determines the initial bubble wall thickness
- **Frost-line height** - distance from the die face to where this solidification takes place is called the frost-line height (film is optically frosting as it becomes cloudy due to polymer crystallization)
- **Stalk** - bubble region below the frost line
- **Bubble diameter and Film thickness** - Above the frost line, where geometry is effectively frozen-in, the terms bubble diameter and film thickness are simply used for those characteristics
6.3.1 BUR and $D_R$

The two main parameters of the process are the blow-up ratio, BUR, and the drawdown ratio, $D_R$ (or DDR).

The BUR is defined by:

$$BUR = \frac{R_f \cdot (\text{Bubble Diameter})}{R_0 \cdot (\text{Die Diameter})}$$

BUR indicates the increase in the bubble diameter over the die diameter. The die gap divided by the BUR indicates the theoretical thickness of the melt after reduction by blowing. Since it is difficult to use calipers on the bubble to measure its thickness unless you knock it down, a more practical formula is:

$$BUR = \frac{0.673 \times \text{Layflat}}{\text{Die Diameter}}$$

Similarly the drawdown ration is defined by:

$$D_R = \frac{V \cdot (\text{taken up speed})}{v_0 \cdot (\text{die extrusion speed})}$$

The final film thickness can be calculated from the blow-up and draw ratios.

$$\text{Final Film Thickness} = \text{initial film thickness} \cdot \frac{\text{die gap}}{BUR \times D_R}$$

A blow-up ratio greater than 1 indicates the bubble has been blown to a diameter greater than that of the die orifice. The film has been thinned and possesses an orientation in the transverse direction (TD).

A drawdown ratio greater than 1 indicates that the melt has been pulled away from the die faster than it issued from the die. The film has been thinned and possesses an orientation in the machine direction (MD).

In practice these numbers are only approximate because the melt swells as it leaves the die gap. The above calculations are made using the die gap dimension because the degree of swell varies with the different resin used, and processing conditions as well.

6.3.2 Film-Blowing Process Models

In order to get an extensive understanding of the film blowing process, we need to build some cases to study closely. However, three models have been developed to analyze and describe the process in details. They are:

- Isothermal Newtonian Model
- Non-isothermal Newtonian Model
Non-isothermal Non-Newtonian Model
The Isothermal Newtonian Model is the simplest but useful case. But the actual film-blowing process is basically non-isothermal, so there come the non-isothermal models for both Newtonian and Non-Newtonian materials.

6.4 Management of Industry and Manufacturing
The profit is the main goal for industry and business, which is dependent on the sales, the cost of raw materials, the human labor expenditure and also the management of the flow the money.

Talk about the balance of production and efficiency. And the most two expensive components in film manufacturing are the raw material and energy. Some tips to improve raw-material and energy usage and suggestions to make operation more productive are provided.

6.4.1 Well manage the PRODUCT CHANGEOVER
It usually takes a long time to change products, particularly when that involves color changes. Keep record of the time needed for the change of the product and always manage the business and production, which means to keep track of the sales, make appropriate plans for production in advance and determine to cut off some non-profitable production lines. Try every
means possible to reduce the change. Also some certain lines can be working to produce specific product.

6.4.2 Regular Maintenance and Cleaning
A typical problem as lines get older is that instruments break and are not replaced. In order to fine-tune the conditions to make product with consistent quality, operator are supposed to constantly maintain the magnehelic pressure gauges, temperature gauges for air rings, barrel and air-cooling coils, extruder motor amperage meters, haul-off nip-pressure gauges.

Dirt inside dies air rings and internal bubble cooling systems stacks can affect TD gauge variation. Surfaces that contact the film must be kept clean of sticky residue. Bubble-sizing cages will destabilize the bubble. Thus regular cleaning is important and needed.

6.4.3 Efficient ENERGY Consumption
Insulate long melt adapter pipes and air-exchange pipes. Not only will this save energy, but it will reduce gauge variation. Un-insulated melt adapter pipes may create melt-temperature variation.

Extruder motors consume the largest amount of energy. Make sure DC motors have brushes that are not worn out and the motors are not overheating, especially at low speeds.

Other motors that turn chill rolls, nip rolls, or winder components use gearboxes and belts or chains. Make sure these connections are not loose or worn out. This will increase energy consumption and cause subtle variations in speed that will affect the machine-direction gauge variation. Remember to maintain gearboxes at the temperature recommended by the supplier. Gearboxes that are too hot will accelerate gear wear. And if they're too cool, they will force the motor to expend more energy than necessary to maintain the correct speed.

References


FIBER SPINNING
by Yunqing Chen

Spinning is one of the most common methods for processing synthetic fibers, especially polymer-based fibers. This technology started to be adopted in industrial field in the 1930s, when nylon was developed by scientists at Du Pont, headed by an American chemist Wallace Hume Caruthers (1896-1937). Later, synthetic fiber industrial bloomed in the 1940s; there was a strong need to understand the fundamental of spinning process in order to improve the productivity and quality of the fibers [1]. Subsequently, studies and researches in this field have been extensively carried out world widely, especially in Japan, and so for, several spinning methods are used commonly, such as melt spinning, wet spinning, dry spinning, and electrospinning, etc.

Fiber spinning involves extrusion of a polymeric liquid through fine holes known as spinnerets [2]. After the liquid has been spun, the resulting fibers are oriented by stretching or drawing out of the fibers. According to the type of spinning that the polymer liquid undergoes, fiber spinning is mainly classified into the following two kinds: melt spinning, solution spinning. Usually, solution spinning has two different types: dry spinning, and wet spinning. Furthermore, for the combination of those two types of solution spinning, dry-wet spinning, we call it gel spinning, which is used to manufacture the fibers with high strength or other special properties. Compared to melt spinning, solution spinning has the advantage in processing high molecular weight polyamides and leading to high tenacity filaments. Alternative to conventional spinning methods (melt, wet, dry), electrospinning technique has been developed in fiber industry. It represents an innovation approach to fiber spinning, when electrical forces on polymer melt or solution surface overcome the surface tension and cause an ejection from an electrically charged jet. The diameter of the fibers produced by this technique is of the order of nanometers.

Generally speaking, there are two types of synthetic fiber products, the semisynthetic (cellulosic) and true synthetic (noncellulosic) [2]. Both of them can be produced by spinning technology, specifically, Polyester, Nylon 6, Nylon 66 and Polyoolefin can be manufactured by melt spinning;
Cellulosic acetate, Cellulose triacetate, Acrylic, Modacrylic, Vinyon, Spandex are usually processed by dry spinning; Acrylic and Modacrylic also can be fabricated by wet spinning. And a lot of polymer materials and naturally occurring materials have been electrospun into nano-fibers. Those spun fibers are utilized in various end uses for apparel, home furnishings, and commercial and industrial applications due to their different properties, such as strength, flexibility, resilience, and abrasion resistance [2, 8].

7.1 Material Feature

Irrespective of the fiber-forming polymers chemical nature, it must possess the following characteristics [2]:

1. **Great length**—at least 200 monomer units must be joined in a chain;
2. **A high degree of intramolecular and intermolecular attraction**, whether through primary chemical bonds or other attractive forces;
3. **The ability to be oriented along the axis of the fiber**;
4. **The ability to form well-ordered crystals or pseudo crystals**.

To be able to spin, all of the manufactured fibers should follow those principles [2]:

1. The fiber-forming material must first be converted into a fluid state, for the thermoplastic polymers, this process is simply melted; for those not, they need to be dissolved in a solvent or chemically treated to form soluble or thermoplastic derivatives;
2. The fluid is forced under pressure (extruded) through tiny holes into a medium which causes it to solidify;
3. The solid fibers are further processed to obtain their optimum properties.

7.2 The Spinneret

When an equipment forces liquid polymers through the spinneret, turn them into long strands and harden them into desirable fibers, the whole process is similar to spiders making silk, so the scientists named this equipment as spinneret (see Figure 1) [1]. In the fiber spinning system, the spinneret is an important part. It is used in the production of all man-made fiber whereby liquid is forced through holes. Filaments emerging from the holes are hardened and solidified. The head of each spinneret represents a point of vulnerability in the system, because the tiny holes can clog with polymers and impurities and render the device useless. Although, for the
different spinning methods the spinnerets are different from each other, basically, the main structure and use is the same.

To start spinning, the polymers should be prepared into liquid substance, either through melting or solvent treatment. As it is forced through tiny holes in the head of the spinneret, the chains in the polymers align, and create long strands. Air or liquid on the other side provides a cooling bath to harden and temper the fibers so they will be usable. For the common spinning of filaments in the finished range of about 0.01~0.05 mm diameter spinnerets of a diameter of 0.05~0.25 mm are used for solution spinning, and 0.1~0.7 mm for melt spinning [3].

7.3 Melt Spinning

Melt spinning (see Figure 2&3) can be used to create fibers for thermoplastic polymers. Based on different shape of holes in the spinneret, melt spun fibers can be extruded in different cross-sectional shapes (round, trilobal, pentagonal, octagonal, and others) to fulfill variety purpose of use. It utilizes a rapid cooling system to transform melted base materials into long strands, or filaments. Melt spinning is commonly used to produce fibers such as nylon, polyester, and acrylic. This process offers a number of advantages to fabric and fiber manufacturers, due to the fact that it can allow fast manufacturing of multiple sorts of fibers with a minimum cost of labor.

In a typical melt spinning application, the polymer is melted with the aid of a screw extruder, and the flow rate of the polymer to the spinneret is governed by metering pumps, which can insure an even flow of polymer into the spinnerets [10]. As the molten polymer passes through a spinneret hole, it is drawn away and attenuated by a draw-down force applied by a take-up roll, and at the same time, the temperature of the spun polymer
decreases rapidly by passing cold air blowers. Depending on the equipment, some of spinning machines may twist multiple strands together to create a thicker fiber or geometric profiles, while some may produce monofilament which usually under a relatively low spinning speeds [5].

![General process diagram for melt spinning](image)

**Figure 2 General process diagram for melt spinning [10]**

The properties of each fiber processed by melt spinning, such as tenacity, modulus, and luster are determined by the spinning speed and temperature, as well as cooling process. That is because, as the molten filament undergoes in spinning procedures, it is orienting the polymer chains and crystallizing the polymer, just like “structuring” the polymer [9].

![Schematic representation of the melt spinning process](image)

**Figure 3 Schematic representation of the melt spinning process [9]**

Despite its many advantages, melt spinning is also associated with a number of limitations. The biggest issue about this process is polymer limitation because of the application only can melt the materials within a reasonable temperature range. The following table shows the typical melt-spun fibers manufacturing parameters.
<table>
<thead>
<tr>
<th>Chemical name of extrudate</th>
<th>Alternative Designation</th>
<th>Melting Point (°C)</th>
<th>Spinning Temperature, (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
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<td>Nylon-6,10</td>
<td>215</td>
<td></td>
<td>Monofilament</td>
</tr>
<tr>
<td>Polyhexamethylenedodecanediamide</td>
<td>Nylon6,12</td>
<td></td>
<td></td>
<td>Monofilament</td>
</tr>
<tr>
<td><em>Polyesters</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>2GT; PET</td>
<td>260</td>
<td>280-300</td>
<td></td>
</tr>
<tr>
<td>Poly(tetramethyleneterephthalate)</td>
<td>4GT; PTMT; PBT</td>
<td>224</td>
<td>240-260</td>
<td></td>
</tr>
<tr>
<td>Poly(1,4-bismethylenehexaneterphthalate)</td>
<td></td>
<td>290</td>
<td>310-320</td>
<td></td>
</tr>
<tr>
<td>Polyoxoacetyl</td>
<td>Polyglycolide</td>
<td></td>
<td></td>
<td>Sutures</td>
</tr>
<tr>
<td>Poly(2-oxyethoxyacetyl)</td>
<td>polydioxanone</td>
<td></td>
<td></td>
<td>Sutures</td>
</tr>
<tr>
<td><em>Polyolefins</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
<td>130</td>
<td>225-300</td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td></td>
<td>170</td>
<td>250-300</td>
<td></td>
</tr>
<tr>
<td><em>Chlorofibers</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinylidene chloride) copolymers</td>
<td>Saran</td>
<td>120-140</td>
<td>175</td>
<td>Monofilament</td>
</tr>
<tr>
<td><em>Polyurethanes</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Novoloid fibers</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol-formaldehyde novolac</td>
<td>kynol</td>
<td></td>
<td></td>
<td>Postcured to form thermoset</td>
</tr>
<tr>
<td><em>Polysulfides</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(p-phenylene sulfide)</td>
<td>Ryton</td>
<td>285</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>
7.4 Wet Spinning

Wet spinning (see Figure 4&5) is another widely used fiber technique. The spinnerets are immersed in tanks containing the coagulation into which the filaments are extruded. Based on three different physicochemical principles, wet spinning also can be divided into three sub methods [1]: the liquid-crystal method, the gel method, and the phase-separation method. The liquid-crystal method uses a formation of a solid crystalline region in the solution when solidify the liquid-crystalline solution of a lyotropic polymer. The gel method uses a formation of intermolecular bonds in the solution when solidify the polymer solution. And phase-separation method involves two different phases appear in the solution, polymer-rich and polymer-lean.

![Figure 4 General process diagram for wet spinning [10]](image)

The process begins by dissolving polymer chips in a suitable organic solvent, such as dimethylformamide (DMF), dimethylacetamide (DMAc), then the spinning solution is extruded through spinneret into a precipitation bath that contains a coagulant (or precipitant) such as aqueous DMAc or water. Finally, the coagulated filaments pass over a guide to driven rollers. The extrusion direction is variable from vertically upwards to horizontal. The spinnerets used in wet spinning can have up to 2,000 holes for commercial applications. However, conventional wet spinning is the slowest of the principal processes having windup speeds to approximately 150 m/min [5].
The coagulation rate has a large impact on the final fibers properties. The wet spinning processing conditions, such as concentration and temperature of the spinning solution, concentration and temperature of the spinning bath can lead the filaments have different physical properties, too. Following table shows the typical wet-spinning solvents and coagulants.
Table 2 Typical Wet-spinning solvents and Coagulants [5]

<table>
<thead>
<tr>
<th>ISO Fiber Class</th>
<th>FTC Fiber Class</th>
<th>Chemical Structure of Fiber</th>
<th>Solvent</th>
<th>Coagulant</th>
<th>Coagulant Concentration, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscose</td>
<td>rayon</td>
<td>cellulose</td>
<td>aqueous solution of sodium salt and xanthate ester</td>
<td>dilute sulfuric acid + sodium sulfate + zinc sulfate</td>
<td>7-10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>modal</td>
<td>rayon</td>
<td>cellulose</td>
<td>aqueous solution of sodium salt and xanthate ester</td>
<td>dilute sulfuric acid + sodium sulfate + zinc sulfate</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>cupro</td>
<td>cupra</td>
<td>cellulose</td>
<td>aqueous cuprammonium hydroxide</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>alginate</td>
<td></td>
<td>calcium salt of alginic acid</td>
<td>aqueous solution of sodium salt of alginic acid</td>
<td>slightly acidic aqueous calcium hydroxide</td>
<td></td>
</tr>
<tr>
<td>protein</td>
<td>azlon</td>
<td>arachin, zein, or casein</td>
<td>dilute sodium hydroxide</td>
<td>dilute sulfuric acid + sodium sulfate</td>
<td></td>
</tr>
<tr>
<td>acrylic</td>
<td>acrylic</td>
<td>copolymer of acrylonitrile</td>
<td>dimethylformamide</td>
<td>50 % aqueous dimethylformamide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&lt;85 wt %) with other monomers</td>
<td>dimethylacetamide (DMA)</td>
<td>50% aqueous dimethylacetamide</td>
<td>17-25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dimethyl sulfoxide</td>
<td>50% aqueous dimethylsulfoxide</td>
<td></td>
</tr>
<tr>
<td>Fiber Spinning</td>
<td>10% sodium thiocyanate</td>
<td>30% zinc chloride</td>
<td>10-15</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------------</td>
<td>-------------------</td>
<td>-------</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30% nitric acid</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30% ethylene carbonate</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15-20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>modacrylic</th>
<th>copolymer of acrylonitrile, acetone, up to 50% acrylonitrile</th>
<th>aqueous acetone</th>
<th>15-25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35-85 wt%, with other dimethylformamide (DMF) &gt;50% acrylonitrile</td>
<td>aqueous dimethylformamide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>_monomers</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>vinylal</th>
<th>poly(vinyl alcohol), posttreated with formaldehyde water</th>
<th>aqueous sodium sulfate</th>
<th>10-18</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aramid</td>
<td>poly(p-phenylene-terephthalamide) 100% sulfuric acid</td>
<td>water or dilute sulfuric acid</td>
<td>20</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------------------------------------------------------</td>
<td>-----------------------</td>
<td>-------</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>elastine</th>
<th>segmented polyurethane DMF DMA 30% aqueous DMA</th>
<th>18-30</th>
<th></th>
</tr>
</thead>
</table>
7.5 Dry Spinning

Similar to wet spinning, dry spinning (see Figure 6&7) is also used for fiber-forming substances in solution. However, instead of precipitating the polymer by dilution or chemical reaction, solidification is achieved by evaporating the solvent in a stream of air or inert gas. A higher viscosity is needed for dry spinning than for wet spinning in order to achieve the necessary polymer concentration needed for spinning [3]. Before the polymer solution passes through the spinneret, it is heated to a temperature above the boiling temperature of the solvent. Then the solution is extruded into a spin cell which is fulfilled with pre-heated gas (air or inert gas) to help vapor the solvent and protect the filaments. The number of holes in the spinneret typically does not exceed 2000. The typical height of a spin cell is 3-10 m tall and the fibers can be wound up at speeds up to 1000 m/min [5]. Table 3 lists the typical dry spinning system, including fiber materials and their corresponding solvent and polymer concentration.

![General process diagram for dry spinning](image)

Figure 6 General process diagram for dry spinning [10]
Figure 7 Schematic representation of the dry spinning process [10]

Table 3 Typical Dry-Spinning Systems [5]

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Solvent</th>
<th>Polymer Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetate</td>
<td>acetone + 2-6% water</td>
<td>20-30</td>
</tr>
<tr>
<td>triacetate</td>
<td>methylene chloride + 5% methanol</td>
<td>20-22</td>
</tr>
<tr>
<td>acrylic</td>
<td>dimethylformamide</td>
<td>25-32</td>
</tr>
<tr>
<td>modacrylic</td>
<td>acetone</td>
<td>25-30</td>
</tr>
<tr>
<td>PVC</td>
<td>carbon disulfide + acetone (40:60)</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>acetone + benzene</td>
<td></td>
</tr>
<tr>
<td>vinyl chloride-vinyl</td>
<td>acetone</td>
<td></td>
</tr>
<tr>
<td>acetate copolymer</td>
<td>acetone</td>
<td></td>
</tr>
<tr>
<td>elastane</td>
<td>dimethylformamide</td>
<td>20-35</td>
</tr>
<tr>
<td></td>
<td>dimethylacetamide</td>
<td>20-25</td>
</tr>
<tr>
<td>Poly (m-phenylene</td>
<td>dimethylformamide + 5% LiCl</td>
<td>15-20</td>
</tr>
<tr>
<td>isophthalamide)</td>
<td>dimethylacetamide</td>
<td></td>
</tr>
<tr>
<td>polybenzimidazole</td>
<td>dimethylacetamide</td>
<td></td>
</tr>
</tbody>
</table>

7.6 Gel Spinning

In gel spinning, the polymer is not in a true liquid state during extrusion. Instead of being completely separated in a solution, the polymer chains are bound together at various points in liquid crystal form. The procedures are
more like a combination of wet spinning and dry spinning, which is firstly the polymer pass through air then cooled further in a liquid bath. Because this procedure provides strong inter-chain forces in the resulting filaments, the fibers can obtain a very high level tensile strength. Therefore, gel spinning is used for fabricating ultra-high strength polyethylene fibers (UHSPE) [1]. Due to the features of this method, high molecular weight polymer solution is requested. The most commonly used materials for this method are polyvinylalcohol (PVA) and poly (acrylonitrile) (PNA).

![Gel Spinning Process Diagram](image)

Figure 8 Schematic representation of the gel spinning process [1]

### 7.7 Electro spinning

Electrospinning (see Figure 9) is well known as the most versatile technique for the preparation of continuous nano fibers. In 1902, Cooley and Morton applied patent for the process of electrospinning, ever since that, the technology has been developed by more than one hundred years. Nowadays, the application is essentially consists of a high-voltage power supply, a grounded collector and a positively charged capillary filled with polymer solution [6]. After the high voltage is applied to the liquid, it gets charged, when the electrostatic charge becomes larger than the surface tension of the polymer solution at the tip of capillary, a liquid polymer jet is formed [6, 7]. Under the action of electrostatic repulsion, the jet is elongated and finally deposited on the grounded collector. This process doesn’t need the use of coagulation chemistry or high temperatures, and ensures no solvent can be carried over into the final fibers. According to different polymer materials, the size of electrospun fiber can be with the diameter between 50 nm and 5 µm. Meanwhile, electrospun fibers have shown many outstanding properties, such as large surface area, high length/diameter ratio, flexible surface functionality, tunable surface morphologies and superior mechanical performance [6].
Figure 9 Schematic representation of the electrospinning process [6]

References


8

**Processing of Thermosets**

by Harris Handoko

**Background**

This chapter seeks to guide the user with a more detailed walkthrough of certain methods that can be used to process various thermosets. The user is assumed to consult various references for specific ways certain resins can be processed. In general, the main steps involved are generally the careful choice of resins and curing agents based on the chemistry. Epoxies, for instance, makes use of primary organic amines as curing agents. These uncured base resins can come in many forms (e.g. liquid, solid). Viscous liquid ones normally need to be preheated to certain temperatures below their curing temperatures, placed in the molds and distributed to take the shape of the cavity all before the curing progresses to a gel point where it will solidify. Being thermosets, the crosslinking binds the polymer chains together in a network that inhibits molecular movements such as reputation. These result in the thermosets ability to resist deformation and are thus usually rigid and brittle. Elastomers are a class of thermosets that take advantage of the crosslinking to regain their original shape.

Each of the processing methods are only suitable for processing certain thermosets, e.g. polyurethanes for reaction injection molding.

**Injection Molding (IM) for thermosets**

Chapter 13 of this book covers a great amount of detail on injection molding and there are other great references available. For the sake of completeness, its basic principles and design will be promptly discussed here with respect to thermosets.
This basic design (see figure 1) consists of two parts: the injection unit and the clamping unit. In essence, the former is like a blender/juicer device (without the pressure involved), comprised of a funnel-like inlet called the hopper where pellets or granules of the resin are fed through into a cylindrical compartment called the screw injection cylinder or barrel that has electrical heating bands. Inside, there is the reciprocating screw in the barrel that rotates and mixes the melting (or increasingly less viscous) resin by shearing forces at a speed of 20-75rpm. The dimension of the screw used is usually shorter for thermoset processing due to their sensitivity to the heat produced during the shearing that can cause premature curing. The screw was a major improvement (in effective pressure) over the older simple plunger setup where resin heating was not homogenous due to lack of mixing action. The melted resin is gradually delivered forward into the front of the screw, pushing it back, before it sends the accumulated resin liquid through the check valve nozzle into the clamping unit using hydraulic pressure. The amount of pressure can vary, but generally tends to be much higher for thermoset resin compounds, estimating on average 200MPa. The clamping unit itself is responsible for delivering the pressure, called the clamping force, needed to keep the mold parts sealed during the holding time where the resin will cure. Depending on the resin type, the molding temperature and holding time will vary.

Injection molding is traditionally a processing method most suitable for only thermoplastics and metals. However, it has been mentioned that it is also possible for thermosets, assuming great care is taken for the following: temperature and cycle timing. Thermoset resins must have sufficiently low viscosities (heated if necessary, or one can simply use those with low molecular weight) at temperatures much lower than the molding temperature to smoothly flow down the runners, pass the gates and into the mold cavities.
where curing at elevated temperatures around 140-170°C will take place. Careless control of these parameters will result in catastrophically untimely curing. Additionally, since there might be additives such as plasticizers, reactive diluents, fillers and fibers in the resin solution, the user must ensure that they do not phase separate throughout the flow. All these could have been more challenging back before the 1970s, but the incorporation of microprocessors using solid-state systems shortly after that period had allowed for more intricate control over the process. With everything computerized, these machines are usually manufactured with sensors and feedback systems to gauge and control, using hydraulics, many parameters such as the speed and position of the reciprocating screw, including mold cavity temperature and pressure as well as resin melt variables. Newer developments, however, have made modifications of this technique to make processing of thermosets easier—reaction injection molding (RIM, see figure 2), along with reinforced reaction injection molding (RRIM), structural foam molding (SF) and sandwich molding (SM), each of them granting certain advantages or improved mechanical properties. Note that RRIM only differs from RIM in that the former uses filled resins (i.e. resins with additives added to enhance properties). SF and SM will not be discussed. The reaction-injection molding (RIM) method was first developed for the polyurethane system. In a nutshell, it involves the simultaneous metered dispensing of two or liquid resin monomers that are stored (and kept warm above room temperature to improve fluid flow) in their respective feeder tanks (see figure 2), into the supply lines that lead to a mixing chamber where the reactants will be mixed quickly before being injected into the mold for curing to take place. Excess reactants will need to be recirculated back to their respective tanks because of certain inevitable mechanical limitations which will be discussed shortly. The mixing itself is accomplished through a high-speed screw or some form of static mechanical mixer for low pressure (older) systems. For high pressure (newer and currently more prevalent) system, mixing is done by the collision of about
10-100m/s jet streams of each reactant referred as the jet-impingement. The mixhead shown in Figure is one of the designs by Keuerleber et al that incorporates a reactant recycling route and was used commercially. How does it work? Each time the reactants are drawn from their tanks at high pressure simultaneously, the cylindrical piston or ram (b) will be raised to just above the mixhead orifices (a), from which each reactant will exit as a high velocity jet stream and collide with each other in the mixing region (d). The problem is, one reactant often lags the other, referred as the lead –lag, which is normally the result of slight differences in their flow rates, thereby causing a few seconds of flow transient. This transience affects the quality of the mixing and this deviation from the stoichiometric balance could result in decreased degree of polymerization, the consumption of reactive groups by side reactions that requires costly purification, and overall inhomogeneity in the final product. To minimize the flow transient effects, the piston plays a role in mediating the mixing by coming down again to interrupt excess flow of reactants. The reactants will enter the grooves (c) along the outer wall of the piston and channeled back to their source. Even so, the design in Figure has flaws—insufficient sealing to prevent mixing of the two reactants. Patents issued to Macosko introduced a newer mixhead design to overcome that problem. Additionally, there are other publications proposing newer mixing/vortexing technologies that could have potential applications in RIM.

Of course, the choice of starting precursor materials (or reactants) will also determine the type of final product and the system conditions needed. For easier reference, the following table has been adapted from another source in categorizing the variables involved in the RIM process using high pressure systems.
### Table 1

<table>
<thead>
<tr>
<th>Variable category</th>
<th>Input variables</th>
<th>Output variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine</td>
<td>Mixhead nozzle size</td>
<td>Stoichiometric ratio, flow rate and degree of mixing of the reactants; fluid</td>
</tr>
<tr>
<td></td>
<td>Mixhead pin speed</td>
<td>pressures and temperatures; gas entrapment; molding temperature profiles</td>
</tr>
<tr>
<td></td>
<td>Mold geometries</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Injection speed</td>
<td></td>
</tr>
<tr>
<td>Chemistry</td>
<td>Reactants</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Catalyst</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fillers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other Additives</td>
<td></td>
</tr>
</tbody>
</table>

The input variables here are analogous to extensive variables, just as the output variables are to intensive variables. Temperature settings of the machinery, mixing speed of the mixers, the angles and dimensions of the molds, reactant types and concentrations, types of catalyst and fillers and additives used are directly determined by the user and independent of any other factors. Each by itself is not a significant indicator of the product’s outcome. Depending on them, however, the actual stoichiometric ratio and quality of mixing of the reactants are some of the important variables that will be affected. Mechanical limitation of the dispensing mechanism to accurately and reproducibly dispense the reactants is likely the one of the causes that leads to stoichiometric imbalance. The same goes for the behavior of the reactant solutions after they are dispensed or the reaction mixture as it is injected into the mold. From this two-pronged classification, it demonstrates the absolute need to balance the roles of the mechanics and chemistry. Literature pertaining to the invention and commercialization of mixheads with multiple injection channels, as well as sequence control are available for reference.

Measuring the degree of mixing of the reactants would call for a rigorous mathematical walkthrough of rheology and fluid dynamics, which is out of the scope of this chapter. A large amount of literature has been dedicated to understanding the actual mixing process of the RIM method, which still remains relatively not fully understood. However, Reynolds number, a dimensionless quantity, is the one most widely used indicator of mixing at this stage, given by
Equation 1: Reynolds number

\[ Re = \frac{\text{fluid density} \times \text{fluid velocity} \times \text{channel crosssection}}{\text{fluid viscosity}} = \frac{\rho v d}{\eta} \]

The equation is principally a measure of the ratio of the tendency of the reactant to assume a turbulent flow that favors mixing, to the laminar flow that does not. Of course, this is specific to each of the colliding reactant jet stream. It is the to the user’s discretion based on experimental findings what criterion value would be considered good mixing or not. In the present context, it is governed by the reactant’s inherent density and viscosity, as well as its jet stream velocity and the diameter of the mixhead orifice. Viscous fluids do not mix well due to limited diffusion, and higher velocity jets result in stronger collision and mixing. A bigger flowing channel will also introduce more movement irregularities, thus contributes to turbulence. The reactant’s temperature must also be taken into consideration as viscosity is largely dependent on it. For further reading pertaining to investigations concerning the quantification of the degree of mixing, the reader is advised to refer to published literature by Kolodziej12,13.

Basics of mold-filling favor smooth laminar flow of the reactant mixture along the runners into the mold cavities, where the so-called flow front (or front tip of the moving mold mixture along a uniform pipe) is expected to follow a U-shape. Excessive flow speeds may disrupt the integrity of the flow and that a sufficiently low Reynolds value is a good guideline to prevent that. Moreover, gas entrainment is an undesirable occurrence and should be removed before complete curing. Below is the reaction time diagram of a typical RIM cure cycle (see figure 4)\textsuperscript{14} showing each step of the process after the reactants have been mixed. Viscosity will exponentially rise with time during filling and curing stages until the gel point is reached, at which solidification occurs and the material properties such as stiffness will increase. The molded product will normally be ejected before it attains its maximum properties. A post-cure will then take place at higher temperatures.

\[ Figure 4: \text{RIM cure cycle after mixing stage, showing the developments of its physical properties over time.} \]
Compression (Press) Molding

Compression molding is one of the most inexpensive processing methods. Since its working principle is very simple, it wouldn’t be surprising for historians to claim that it might have a very ancient origin. Its successful application as a manufacturing process only gained much attention during the late 1800s: Thomas Hancock improved on the process of rubber compression molding. It was primarily the method for processing thermosets, but it has also been used to process thermoplastics and elastomers. Depending on the type of material and end product, there are slight differences to the method. Some of the composite constituent materials processed with compression molding include sheet molding compounds (SMC), bulk molding compounds (BMC), Glass mat reinforced thermoplastics (GRT) and long fiber reinforced thermoplastics (LFT).

This process is perfect for moderate to large-volume manufacturing and is capable of producing molded parts with excellent strength and shape-complexity. It works as follows: (1) some metered amount of molding compound (or so-called a ‘charge’) is placed within the lower half section of an open, heated (~140-170°C) mold cavity, (2) matching upper half section of the mold is lowered with hydraulic pressure up to a few thousand psi to enclose the cavity, forcing the molding compound to fill up and completely take the shape of the mold, while any excess will be evicted out and pressure is held for the duration of the cure time (a few minutes), (3) finally, cured compound is removed by knockout pins. The excess eviction in part (2) is called flashing and these ‘extras’ should be removed. The molding compound comprises the resin and other additives. The advantage of this process is the easy inclusion of many additives such as fillers, catalyst, accelerators, lubricants and colorants to the resin to enhance properties and processibility. Thickeners, flame retardants and UV absorbers are also some additives that give specialized properties as demanded by some

\[\text{Figure 5: Compression molding press. (1) Charge in mold cavity, (2) upper mold piece lowered and held with pressure for duration of cure time, (3) cured compound is ejected}\]
applications. Molding compounds, depending on the resin type and additives added, have a limited shelf-life called the pot life.

In order to improve production efficiency, the temperature of the molding compound may be pre-adjusted higher so as to reduce curing time in the cavity.

In reference to figure 5, mold presses have significantly changed over the decades in terms of operations controls. Where temperature and pressure parameters of the machine used to be steam-driven, most of the variables such as platen temperatures that heats up the molds and the hydraulic pressure are now automated and controlled electrically. A few things to note are that compression mold presses are normally of vertical design and come in either downstroke or upstroke stamping mechanism. The former is normally used for high pressures.

Three kinds of molds exist for this process (see figure 6) namely, the positive, semipositive and flash molds—each suitable for producing different products. For instance, the flash mold (A) works by a careful press (to avoid gas entrainment) on a slight excess of molding compound within the mold cavity. Because low pressure is used here, only molding compounds with high melt viscosity is suitable for using this mold, such as rubbers melts. The high melt viscosity of the compound induces pressure within the mold when shut. This kind of mold produces lower density products due to the low pressure used and is generally wasteful, but it is cheap. A positive mold, on the other hand, requires accurate measurement of the molding compound within the cavity as the molding compound receives the full pressure and no breathing room exists between the upper mold section (or plunger) and the cavity, prohibiting escape of the compound and trapped air—causing defects and variations in thickness between batches due to differences in measured ‘charge’. This is normally an undesirable mold choice. The semi-positive mold, incorporates a little bit of both. It has breathing room to allow flashing of excess compound and for gas removal. There is a ledge within the mold cavity for the upper mold piece to rest on, thus ensuring a constant cavity...
volume. By allowing gas to escape, the appearance of ‘blisters’ in the product will be eliminated. Semi-positive molds are, however, more expensive but the quality of the processed products justify the cost.

**Transfer molding** is a newer method of compression molding. The main advantage over the conventional compression molding is its ability to make products with intricate designs. There are essentially three key aspects to the design: the transfer plunger, the transfer pot and the connecting runners that lead to the actual mold cavities. To begin, the molds are already in a closed position. A measured amount of the molding compound (in the form of powders or viscous liquid) is placed inside the transfer pot that has heating elements to melt or reduce the viscosity of the compound for smooth flow. When sufficiently heated, the fluid will flow into the runners and enter the cavities where enough time will be given to cure at temperatures around 140 – 170 C. Once cured, the mold will be disassembled to retrieve the products and the disc-shaped cured material remaining in the transfer pot called the ‘cull’ can be discarded. Since mold piece inserts are often used to make the more delicate small parts and that molding compound is usually in some powdered form, this design poses less chance of damaging or displacing the inserts. Apparently, this design also has the benefit of efficient heat transfer based on curing studies of epoxy molding compounds (EMCs). As with everything, good things don’t come cheap. Better precision tools will cost more, including maintenance. This technique also introduces some degree of structural orientation due to the extrusion-like effect caused by a pushing the compound through orifices.

**Autoclave curing**

Autoclave curing is actually a subset of vacuum-bag molding process. As the name suggests, the process involves airtight enclosure of a mold cavity
that has the molding material in place and then applying vacuum such that the flexible rubber bag will ‘deflate’ and press the molding material against the mold cavity shape (see figure 8).\(^{18,19}\) There is referred as a low pressure process for the fact that no pressure was actually being used! The molding material in this case is normally reinforcing fibers (e.g. glass) impregnated with the thermosetting resin material. This method is especially used also in the preparation of thermosetting composite laminates. The autoclave curing methods basically implements the use of an autoclave pressurized vessel so that higher pressure maybe achieved on the outside as well. Figure 9 shows a complex laminate structure that has layers of films, fabrics and plates, etc. This also speeds up the curing process.

![Figure 8: Vacuum-bag molding. (a) Before applying vacuum, (b) after applying vacuum](image)

![Figure 9: Autoclave process of laminate structure. (a) Vacuum bag, (b) compression plate, (c) pressure-distributing layer, (d) perforated release film, (e) absorbent material, (f) release film or fabric, (g) peeling film, (h) fiber-composite laminate, (i) release film, (j) mold, (k) sealing compound, (l) mold boundary, (m) double gasket](image)
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9

Compression Molding
by Hong Lu

Compression molding is one of the most important methods for processing. It is widely used to process thermosetting systems and difficult-to-process thermoplastics. Compression molding has the advantages of low cost, low molding pressure, low fiber breakage and dimensional accuracy. This paper is going to give an overview of the compression molding for the background, basic processing procedures and anomalies may occurs during the mold filling.

9.1 Historical Background

To mold an artifact by pressing, compression into a shaped cavity is the oldest process used in manufacture polymer products. The first known screw presses were mentioned by the Greeks about 200 B.C.E. Later during the Civil War, the typical compression molding had been used to molded out of natural rubber as Figure 9.1 presents. In 1926 L.E. Shaw invented the transfer compression molding process, which is used for thermosetting materials. It is similar to the ones we used nowadays. The charge is placed inside a cavity for heating, and then apply high pressure to soften the materials in order to flow through the sprue and get into the mold cavities. After Shaw’s invention, many compression molding machines were transformed into different types.
9.2 Introduction

The essential features of the compression molding process are illustrated in Fig. 9.2.
There are various types of compression molding parts and processes, for example, according to the type of materials used, etc. However, in this paper we are going to concentrate on four most commonly used processes: the compression molding of sheet molding compound (SMC), the injection-compression molding of bulk molding compound (BMC), the compression molding of glass mat reinforced thermoplastics (GMT) and long fiber reinforced thermoplastics (LFT). SMC and BMC are fiber reinforced thermosetting materials, the common matrix in SMC and BMC materials are unsaturated polyester, cross-linked with styrene. While GMT and LFT are fiber reinforced thermoplastics, polypropylene is one of the most common matrix for them. Table 9.1 presents some materials that are commonly found in compression molded products.

**TABLE 9.1 Typical Resins Found in Compression Molding**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene rubber</td>
<td>BR</td>
<td>Elastomer</td>
</tr>
<tr>
<td>Epoxy</td>
<td>EP</td>
<td>Thermoset</td>
</tr>
<tr>
<td>Ethylene-propylene-diene rubber</td>
<td>EPDM</td>
<td>Elastomer</td>
</tr>
<tr>
<td>Melamine-formaldehyde</td>
<td>MF</td>
<td>Thermoset</td>
</tr>
<tr>
<td>Nature rubber</td>
<td>NR</td>
<td>Elastomer</td>
</tr>
<tr>
<td>Phenol-formaldehyde (phenolic)</td>
<td>PF</td>
<td>Thermoset</td>
</tr>
<tr>
<td>PF mineral-filled moldings</td>
<td>PF-mf</td>
<td>Thermoset</td>
</tr>
<tr>
<td>PF organic-filled moldings</td>
<td>PF-of</td>
<td>Thermoset</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>PA6</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polyamide 66</td>
<td>PA66</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polypropylene copolymer</td>
<td>PP-CO</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>PTFE</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PUR</td>
<td>Thermoset</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>SI</td>
<td>Elastomer</td>
</tr>
</tbody>
</table>
BMC and SMC have been widely used in industry. There are lots of applications for compression moldings. The main areas are automotive, electronics, household goods. Figure 9.3 presents the percentage of different areas of BMC and SMC materials in North America for 2002. The automotive industry is the largest user of SMC/BMC materials.

9.2 Compression Molding of SMC and BMC

The compression molding process of SMC is schematically depicted in Figure 9.4. Firstly, the charge is placed in the open heated mold cavity as (1), then the mold is closed and compression begins with pressure, as (2) and (3). The pressure and heat should be maintained until the molding material has completely cured. Finally the mold opening, part could be removed. Among these procedures, the dominant event is the curing process.

The compression molding of BMC is very similar to SMC. The material is compounded into an internal mixer and then fed into the cylinder for pressure to extruded into the shape we want to.
9.3 Compression Molding of GMT and LFT

The processing of glass mat reinforced thermoplastics are as the followings: Firstly charge is placed on the conveyor belt to go through the heating unit. Then heating the charge. Heating ways could be radiative heating, contact heating, convective heating, or a combination of all above. Then the charge is paced on the cool mold. When the cavity is full, the part is cooled under pressure. Once it is cooled sufficiently, the part is removed and the process is finished. The difference between GMT and SMC is that the dominant event is the heating part. The compression procedure is under the condition of cooling rather than heating. Also GMT do not need to be cured as the materials are thermoplastics.

LFT is a method that comes from resent years. The process is very similar to the GMT. Usually the LFT charge is processed by extruder. Then the charge is putted on the mold cavity. One thing should be noticed is that long fiber reinforced pellets have to be prepared by coating, extrusion, or pultrusion. But there is one draw back of LFT system: the fibers will suffer significant damage during the extrusion process.

9.4 Material preparation

Before the compression molding precess begins, there are some certain procedures need to be done. The materials should be weighted first, then cutting into small pieces, and finally placing to the cavity. The three procedures mentioned above usually finish by hand. If the materials are thermoplastics, preheating is needed. Because at room temperature, thermoplastics do not flow. So before compression, the materials’
temperature should be heated above the melting temperature. While for thermostetting materials, charges are usually placed on the mold at room temperature, or later being heated for a few seconds. Because thermostets could create a network of bonding. Once thermoset in connect with the mold, they become soft and viscous, a thin layer comes into beings at the mold surface which moves downward.

9.5 Compression Molding Variables

Table 9.2 contains some important variables for compression molding. The first four items are all dependent on the press setup, and generally they are outside the influence of the press operator. While the last four items are relatively to the press operator.

<table>
<thead>
<tr>
<th>Table 9.2 Important Molding Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Press slow close</td>
</tr>
<tr>
<td>2. Molding Pressure</td>
</tr>
<tr>
<td>3. Mold Temperature</td>
</tr>
<tr>
<td>4. Cure Cycle</td>
</tr>
<tr>
<td>5. Charge Size</td>
</tr>
<tr>
<td>6. Charge Weight</td>
</tr>
<tr>
<td>7. Charge shape</td>
</tr>
<tr>
<td>8. Charge placement</td>
</tr>
</tbody>
</table>

Press show close plays a more important role in BMC and SMC than GMT and LET. If the slow rate is too fast, the closure will have air entrapped. If the slow rate is too low, the material is going to pregel on the hot mold. Molding pressure also will affect the properties of the materials. Lower pressures tend to cause scumming of the mold and porosity. Higher pressure can increase sink marks. Usually the range of pressure is 2000-3000 psi. Molding temperature depend on some particular resin-catalyst system we used. To have a reasonable cure cycle, most materials are molded at nearly 300°F to 375°F. The temperature of female portion is
usually 10 °F hotter than the male portion. The range of temperature should be with ± 10 °F. To achieve those goals, the mold must be designed for good heat transfer property. The minimum cure cycles are desirable. For SMC and BMC, over cure contributes to parts sticking in the mold and to slight surface crazing. Depending on the size, weight, thickness and type of matrix, the curing time should be ranged.

While the last four variables about charge selecting are not quite simple, which have to based on past experience. Determining the proper charge size is the most complicated one. For BMC charge, the larger diameter of the log which is processed by extruder, the less loss of physical properties due to the fiber degradation. Charge shape depends on the geometry of the part, which can be adapted to fit the shape of the mold. For several years experience, small plugs of BMC should not be stuffed into bosses.

9.6 Mold filling

The heart part of the compression molding process is mold filling. The properties of the materials are strongly influenced by the mold filling process. There are several anomalies that may occur during mold filling as the followings.

9.6.1 Fiber-Matrix Separation

When the materials are heated, they must flow around the cavity which has sharp corners. What’s worse, there are some places difficult to access for molding materials, such as rib and boss. While the materials are forced to flow into these area under the pressure, some of the fibers can not easily get into these places, so there are more resin and less fibers in these areas. Just as the Figure 9.5. The results is that the mechanical properties decrease in the sharp or narrow spaces. For example, In cracks at the bottom of the rib, the stress is lower than the level we expected.

![Fiber-matrix separation during mold filling](image)

To avoid fiber-matrix separation, mold filling methods should be noticed. For the variables we discussed above, there some rules we could take into
considerations. Usually a faster closing speed will reduce the fiber-matrix separation, for the reason that slow closing speed allows the resin to seep through the bed of fibers, but high speed will have a smaller effect for that.

### 9.6.2 Preferential Flow

Preferential flow is a phenomenon occurs during the compression molding of thermoset charges. If the heated layer has a low viscosity, in the places near the mold wall, some materials are squeezed out from the charge. Because the loss of materials, there are some voids in the rest finished product. As the figure 9.6 presents. (b) is the situation of preferential flow. (c) shows the voids in the rest materials. This low phenomenon has been seen by Marker and Ford and Schmelzer. This experiments were repeated for several times. To reduce the chance of preferential flow happens, the viscosity should be increased.

![Figure 9.6](image)

**FIGURE 9.6**
Preferential flow of resin rich material flowing ahead of flow front.

### 9.6.3 Knitline Formation

Knitline formation is a common phenomenon when two separate streams of plastic meet in the cavity and meld together, and a V-notch come into beings. Figure 9.7 illustrates this anomalies. It is because that when the two flow fronts meet, the air will create a dimple for the surface of both part.
The dimple may have the shape of V-notch, this structure can lead to a stress concentration.

Usually this phenomenon is caused by air and hot temperatures, and knitlines could happen when multiple charges are placed inside the mold cavity at one time.

![Image of knitline](image.png)

**FIGURE 9.7**
A through thickness view of two flow fronts approaching one another to form a knitline and blemish at part’s surface.

## 9.6.4 Race Tracking/Flow Hesitation

Race tracking occurs as the materials flow along the regions with different thickness. When the compound flow through the mold cavity, they are going to pass the path with smallest resistance. These regions will be more thickness than the others, as the figure 9.8 shows. Because most parts are designed with different wall thickness, it is easy for race tracking happen.
9.7 Outlook

Compression molding is a useful method for processing fiber reinforced plastics. The benefits of compression molding are low cost, fewer knit lines on final product and could produce more intricate parts. The products made with compression molding can be found in nearly every industrial areas. Even there are some anomalies for the materials, it is still provide us a good way to processing materials.
References

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10

Process design of Polymer/Inorganic composites as tissue engineering scaffolds

by Dandong Wang

10.1 Background

“A biomaterial is a nonviable material used in a medical device, intended to interact with biological systems.” (Williams, 1987) Biopolymer composites as a member of biomaterials have gotten more and more attention due to their proper properties, such as biodegradable properties, mechanical properties and processing abilities and so on. In a report published by The Institute of Materials, London, in 1995, the estimated world market for all the medical devices, was in the region of $100 billion/year. Biomaterial as part of it was estimated to around 12% of all, which has increased a lot these years. Biomaterials are expected to perform in our body’s internal environment, which is very aggressive, thus we should consider not only the tough microenvironment in our body, but the biodegradable properties will also be an important factor. For example, the PH of body fluids in various tissues varies in the range from 1 to 9. The tendons and ligaments experience peak stresses in range 40-80 MPa versus 4 MPa has to be loaded on the bones during daily activities. The mean load on a hip joint can be up to 10 times body weight during jumping.

A large number of polymers such as polyethylene (PE), Polyurethane, polyterafluoroethylene, polyacetal, polymethylmethacrylate, polyethylene terethalate, silicon rubber, polysulfone, polyetheretherketone, poly (lactic acid), and poly (glycolic acid) are also used in various biomedical applications. HA/PE, silica/SR, carbon fiber/ultra high molecular weight polyethylene, carbon fiber epoxy, and CF/PEEK are examples of polymer composite biomaterial. Each type of material has its own positive advantages which particular suitable to specific situation.

Since the availabilities in a diverse array of compositions, properties, and forms (solids, fiber, fabrics, films, and gels) and possibilities of fabricating into complex shapes and structures, a large amount of polymers are widely
used in various applications. However, they tend to be too flexible and too weak to satisfy the mechanical demands of certain applications such as joint or bones. Metals have well-known high strength, ductility, while they will be very weak in excited environment and also induce inflammatory reaction due to metal ions. Ceramics are known for their stability in various environments, but brittleness and hard fabrication will be their drawbacks. Polymer composite materials provide alternative choice to overcome these shortcomings of homogenous material mentioned above.

Today, materials used for scaffolds could be divided into two categories: (1) natural or synthetic polymers such as polysaccharides, poly(a-hydroxy ester), polylactic acid(PLA), polyglycolic acid(PGA), polyhydrides. (2) bioactive ceramics such as calcium phosphates and bioactive glasses or hydroxyapatite(HA). In addition, some researchers has been investigated the drug delivery capacity, enhance bone ingrowth to treat bone defects and wound healing with developed scaffolds. The scaffold as a natural composite material provides a framework and initial support for the cells to attach, proliferate and differentiate, and form an extracellular matrix (ECM). One of the most important targets as a scaffold should be able to mimic structure and properties of human tissue to process tissue formation. There are also some vital factors should be considered: (1) an extensive network of interconnecting pores so that cells can migrate, multiply and attach the scaffold. (2) oxygen, nutrients and wastes could be easily transported and carried away. (3) biocompatibility for cells attachment and proliferate. (4) shape (5) mechanical properties and biodegradation profile. This paper will provide a brief review about design and fabrication of polymer/inorganic composite scaffolds.

10.2 Material

10.2.1 Biodegradable polymer matrices

The basic requirements for biomaterials used for scaffolds are their biocompatibility and proper surface properties for cellular attachment, proliferation and transformation. There are two types of scaffold materials, one is natural polymers and the other is synthetic polymers.

10.2.1.1 Synthetic polymers

The advantages of synthetic biopolymers are general and reproducible mechanical and physical properties such as shear strength, elastic modulus and degradation rate. What’s more, the purity of polymer could also be
controlled in fabrication procedure. While the drawbacks such as uncertainty of toxicity and immunogenicity will be their limitation to widely use.

These polymers contains PLA, PGA and their copolymer, poly(DL-lactic acid-co-glycolic acid)(PLGA). Due to their biocompatibility, ability of manufacturing into variety of shapes including 3-Dimensional formation and support strength needs for diverse array of applications, they have played a significant role in various fields. Their hydrolytic degradation through de-esterification property allows them removable after degraded to the monomeric components. And their bodies already contain highly regulated mechanisms for completely removing monomer components. While their weak resistance to the erosion process will lead to failing prematurely, and rapid release of acidic degradation products will cause inflammatory responses. Processing history, molar mass, environment chemical conditions and their own physical conditions are all their important factor affects degradation.

Other important synthetic biodegradable polymers include poly(ortho ester), PCL and polyanhydrides. These polymers also have appropriate biodegradable properties. PCL could combine with HA scaffold do not show a local decreased PH value as commonly observed in PLA. Poly(ortho ester), polyanhydrides belong to a family that undergoes a polymer-water interface dominated hydrolysis process.

10.2.2.2 Natural polymers

Natural polymers always have excellent biodegradable and cellular attachment properties which give them a priority than synthetic polymers.

Collagen, a common kind of natural polymer, is a fundamental protein of vertebrates which exist in tendons, dentals, bones. According to different body conditions, their primary structure and molecular folding, they are divided into 26 distinct types. Type I collagen is the main constitutional part of bone. Type II collagen found in cartilage and type III collagen in blood vessel walls all have excellent biocompatible properties. However, its poor mechanical properties (E~100 MPa) will be disadvantage to widely use. Bovine collagen are the most commonly used type, while it may elicit serious antigenic responses.
10.2.2 Ceramic Phases

Because of the biopolymers’ mechanical limitation, combining biodegradable polymers and bioactive ceramics to make a variety of composite materials has been a good choice for tissue engineering scaffolds. Hydroxy carbonate apatite (HCA) layer as ceramic surface provides the bonding interface with tissues. And HCA, which can bioactive implants, play a similar role as mineral phase in bone. Typical mechanical properties of the bioactive ceramic phases are indicated in the table 1.  

<table>
<thead>
<tr>
<th>Ceramics</th>
<th>Compressive strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Fracture toughness (MPa √m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite (HA)</td>
<td>&gt;400</td>
<td>~40</td>
<td>~100</td>
<td>~1.0</td>
</tr>
<tr>
<td>45S5 Bioglass6</td>
<td>~500</td>
<td>42</td>
<td>35</td>
<td>0.5-1</td>
</tr>
<tr>
<td>Glass-ceramic/A/W</td>
<td>1080</td>
<td>215</td>
<td>118</td>
<td>2.0</td>
</tr>
<tr>
<td>Porous bioactive glass70S30C</td>
<td>2.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Porous Bioglass6-derived glass-ceramic (&gt;90%)</td>
<td>0.2-0.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Porous HA (82-86%)</td>
<td>0.21-0.41</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cortical bone</td>
<td>120-180</td>
<td>50-151</td>
<td>12-18</td>
<td>6-8</td>
</tr>
<tr>
<td>Cancellous bone</td>
<td>4-12</td>
<td>—</td>
<td>0.1-0.5</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 1

Due to its possibility of controlling a range of chemical properties, bioactive glasses have been used as a scaffold material. However, it was reported that crystallization of bioactive glasses decreased the level of bioactivity and even turned them into inert material. Also their compressive strength is very attractive. HA and related calcium phosphates have been intensively investigated as the major component of scaffold material for bone tissue engineering since 60wt% of bone is made of HA. Therefore, HA is superior to the other inorganic material in biocompatibility aspect. However, because porous HA has very poor mechanical properties after comparing with cortical bone, calcium phosphates alone could not be used for scaffold. Instead, they should be combined with collagen fibers to make better scaffold material.

10.3 Processing design for composite scaffolds with interconnected pores

Two or more types of materials combined to suit better mechanical and biocompatibility demands of the host tissue has become a trend in composite scaffold material field. By taking advantage of the formability of polymers and including controlled-volume fractions of a bioactive ceramic phase, mechanical reinforcement of the fabricated scaffold can be achieved. A
variety of dense and porous scaffold composites including their physical properties is given in the table 2, which represent typical systems reported in the literature.

<table>
<thead>
<tr>
<th>Ceramic composite</th>
<th>Percentage of ceramic (%)</th>
<th>Porosity (%)</th>
<th>Pore size (μm)</th>
<th>Compressive (C), tensile (T), flexural (F) strength (MPa)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dense composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA fibre</td>
<td>2–10.5 (vol.)</td>
<td>—</td>
<td>—</td>
<td>45 (F)</td>
<td>1.75–2.47 × 10⁹</td>
</tr>
<tr>
<td>PLLA</td>
<td>10–70 (wt.)</td>
<td>—</td>
<td>—</td>
<td>50–60 (F)</td>
<td>6.4–12.8 × 10⁹</td>
</tr>
<tr>
<td>HA</td>
<td>40–85 (vol.)</td>
<td>—</td>
<td>—</td>
<td>22 (F)</td>
<td>1.1 × 10⁹</td>
</tr>
<tr>
<td>β-TCP</td>
<td>75 (wt.)</td>
<td>—</td>
<td>—</td>
<td>51 (F)</td>
<td>5.18 × 10⁹</td>
</tr>
<tr>
<td>PLLA-ω-PEH</td>
<td>25 (wt.)</td>
<td>—</td>
<td>—</td>
<td>7.5–7.7 (C)</td>
<td>191–134</td>
</tr>
<tr>
<td>A/W</td>
<td>10–50 (vol.)</td>
<td>—</td>
<td>—</td>
<td>18–28 (B)</td>
<td>0.9–5.7 × 10⁹</td>
</tr>
<tr>
<td>Cortical bone</td>
<td></td>
<td></td>
<td></td>
<td>50–150(T)</td>
<td>12–18 × 10⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>130–180 (C)</td>
<td></td>
</tr>
<tr>
<td>2. Porous composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous CaP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>28–75 (wt.)</td>
<td>75</td>
<td>&gt;100</td>
<td>0.39 (C)</td>
<td>10–14</td>
</tr>
<tr>
<td>PLGA</td>
<td>59 (wt.)</td>
<td>85–96</td>
<td>100–1000</td>
<td>0.07–0.22 (C)</td>
<td>2.7–5</td>
</tr>
<tr>
<td>PLGA</td>
<td>60–75 (wt.)</td>
<td>81–91</td>
<td>800–1000</td>
<td>1.5–3.9 (T)</td>
<td>137–260</td>
</tr>
<tr>
<td>PLGA</td>
<td>30–40</td>
<td>43</td>
<td>110–150</td>
<td>0.42 (C)</td>
<td>51</td>
</tr>
<tr>
<td>PLGA</td>
<td>20–50</td>
<td>77–80</td>
<td>~100 (macro)</td>
<td>0.07–0.08 (C)</td>
<td>65</td>
</tr>
<tr>
<td>PLGA</td>
<td>0.1–1 (wt.)</td>
<td>94</td>
<td>~100 (macro)</td>
<td>0.07–0.08 (C)</td>
<td>0.65–1.2</td>
</tr>
<tr>
<td>PDLLA</td>
<td>5–29 (wt.)</td>
<td>93–97</td>
<td>~100 (micro)</td>
<td>0.07–0.08 (C)</td>
<td>0.075–0.12</td>
</tr>
<tr>
<td>PLGA</td>
<td>40 (wt.)</td>
<td>95.5–95.2</td>
<td>98–154</td>
<td>0.075–0.12 (C)</td>
<td>100–500</td>
</tr>
<tr>
<td>Cancellous Bone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2

10.3.1 Solvent casting and particle leaching

Solvent casting (particle leaching) has shown promise for its ability to fabricate scaffolds in room temperature. Solvent casting of biocomposite scaffolds involves the dissolution of the polymer in an organic solvent, mixing with ceramic granules, and casting the solution into a predefined 3D mould. Then solvent is subsequently allowed to evaporate. The primary advantages: (1) controlled porosity after processing, (2) controlled interconnectivity if particles are sintered. The main disadvantages of solvent casting: (1) the limitation in the shapes; (2) the toxicity could not predict after fabrication; (3) the organic solvent may reduce the activity of bioinductive molecules.⁹

Polymer-ceramic constructs can also fabricated by the solvent aggregation method. The polymer microspheres are first formed from traditional water oil/water emulsions. Solvent-aggregated polymer-ceramic scaffolds can then be constructed by mixing solvent, salt or ceramic granules, and pre-hardened microspheres.¹⁰
Little work has been done on producing scaffolds by leaching method. Achieving pore interconnectivity at low porogen loadings is its limitation for applying.

### 10.3.2 Microsphere sintering

This process uses emulsion/solvent evaporation technique to synthesize microspheres of a ceramic and polymer composites. Then sintering the composite microspheres yields a 3D, porous scaffold.\(^{11}\)

Through a water-oil-water emulsion technique, PLAGA-Bioglass composite microspheres could be obtained. Sintering of the microspheres into cylindrical shapes resulted in a well-integrated interconnected porous structure, with the microspheres joined at the contact necks. Average porosity was 40% with pore diameter of 90 \(\mu\)m, and mechanical properties close to cancellous bone. Moreover, bioglass reinforcement gave a two-fold increase in compressive strength. The scaffolds have shown to support the adhesion, growth and mineralization of human osteoblast-like cells in vitro. Advantages of sintering: (1) graded porosity structures possible and controlled porosity easily; (2) can be fabricated into complex shapes. In contrast, the disadvantages cannot be ignored, they are issues about interconnectivity and use of organic solvents.

### 10.3.3 Phase separation

Thermally induced phase separation(TIPS) can produce 3D resorbable polymer scaffolds with very high porosities(~97%) by controlling macro- and microstructures. These scaffolds could be suitable for tissues such as nerve, muscle, tendon, ligament, and teeth.\(^{12}\)\(^{13}\) Their pore morphology, mechanical properties, and biodegradable rates all depend on polymer concentration in solution, volume fraction of secondary phase, quenching temperature and the polymer and bioceramic type as discussed in the former parts.

Simply, the polymers is dissolved in dimethylcarbonate and stirred overnight to obtain a homogeneous polymer solution. A given amount of glass or ceramic powder can be added into the polymer solution. The mixture transferred into a flask and sonicated. After that, the flask is quenched in liquid nitrogen and maintained at -196 °C for 2 hours. The frozen mixture is then transferred into a cool bath at -10°C for 48 hours and then at 0°C for 48 hours, followed by drying at room temperature in a vacuum oven until reaching a constant weight.\(^{14}\) Maquet et al.\(^ {15}\) developed a high porous PDLLA/Bioglass® composite scaffolds prepared by TIPS with
macropores with ~100um, interconnected with macropores in diameter in 10-50um as shown in Fig 1.\textsuperscript{16}

Figure 1 Thermal induced phase separation

Polymer matrix composite films containing nanosized titania and other inorganic particulate inclusions have demonstrated enhanced cell adhesion and a tendency to increased Ca-containing mineral deposition.\textsuperscript{17}

Advantages of this method: (1) high porosities (~95%) and highly interconnected pore structures; (2) Anisotropic and tubular pores possibility; (3) ability of control of pores size and structure by different preparation conditions. Disadvantages: (1) long time and complicate fabrication method; (2) shrinkage issues and limitation of scale; (3) use of organic solvent which could induce inflammatory reactions.

10.3.4 Solid freedom form

Solid freedom form (SFF) known as rapid prototyping provides excellent control over scaffold external shape and internal pores interconnectivity and geometry. Recently, direct SFF fabrication is capable of producing global-pores with minimum feature size of 100 um.\textsuperscript{18} SFF consists of manufacturing a 3D part in a layered fashion based on a computer representation. The part, which can also be used as a mold to cast the final product in indirect SFF manufacturing, is often post processed to yield the final project.
Various SFF have been developed over past 20 years since the advent of stereolithography in 1986. These techniques includes: (1) fused deposition; (2) stereolithography (SLA); (3) Selective laser sintering (SLS); (4) 3D printing. And their superior and drawbacks are indicated in table 3.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereolithography</td>
<td>Hydrogel materials, high-resolution and accuracy, liquid build material can easily be removed from within complex scaffolding</td>
<td>Limited choice of materials, may require furnace postprocessing (e.g. bioceramics), high material cost, complex and expensive equipment</td>
</tr>
<tr>
<td>Laser sintering</td>
<td>Wide range of material choices, good mechanical properties, lower material cost, good accuracy</td>
<td>Materials may thermally degrade during the process, undesired porosity, hard to remove trapped powder, complex and expensive equipment</td>
</tr>
<tr>
<td>3D printing</td>
<td>Wide range of material choices, low cost, quick process, multmaterial capabilities through multi print-heads</td>
<td>Hard to remove trapped materials, low to Medium resolution, powder particles may not bind well, binders are always necessary to bind powders</td>
</tr>
<tr>
<td>Fusion deposition modeling</td>
<td>No trapped materials, minimal material waste, low cost</td>
<td>Materials may thermally degrade during the process, lower range of material choices, medium resolution</td>
</tr>
</tbody>
</table>

Table 3

**Stereolithography.** SLA utilizes the ability of photopolymerizable liquid polymers to solidify when ultraviolet light is focused on the surface of the liquid. A platform supporting the developing model is brought near the surface of a liquid vat, and a UV laser is used to solidify the first cross-sectional layer of the model to the platform. By lowering the platform one cross-sectional layer thickness, recoating the liquid on top of the first layer, then passing the UV light over the new liquid layer, a second layer is deposited. The process is repeated layer by layer until completion, after which the prototype is typical cleaned and completely cured by placing it in an ultra-violet oven.¹⁹

**Selective Laser Sintering.** In SLS, parts are made by passing a laser over a thin layer of polymer powder. The laser will raise the temperature of the powders, which will cause neighboring particles to fuse together both laterally and to the preceding layer below. After a layer of polymer is fused, an elevator platform supporting the part is lowered by the height of the next layer and a roller applies new powder over the previously processed layer. Post processing of the final part can include dissolving out unsintered particles to leave microporosity within the structure. HA and calcium phosphate with a polymer binder have been used in SLS as possible implant materials.²⁰ The ability to directly sinter biocompatible material without high temperature post-processing step gives SLS inherent material advantages over SLA.

**3D Printing.** This technique uses ink-jet printing technology to precisely place a ‘binder’ solution on a bed of powder, thus gluing the powder together in a cross-sectional layer, much as the lasers in SLS use heat to binding powder layers. A platform is lowered and more powder is deposited and processed in layer by layer fashion. The unbound powder in the void spaces of the prototype can then be removed by compressed air or by manually brushing it away.²¹
**Fused Deposition Modeling.** Fused Deposition molding uses a small temperature-controlled orifice to extrude filament material and deposit semimolten polymer onto a platform, which immediately solidifies. At the end of the deposition of each layer, the platform is lowered so that the next layer can be deposited. By changing the direction of each layer and the spacing between materials, scaffolds with highly uniform internal structures are obtained. 22

Above all, the advantages include porous structure, possibility of protein and cell encapsulation, and good interface with medical imaging give it superior to other methods. And the cost is its limitation.

**10.4 Summery**

Due to their bioactive behavior, adjustable biodegradable and proper mechanical properties, the synthetic polymer/inorganic composites are particularly attractive as tissue engineering scaffolds. While from the figure 2, the mechanical integrity of man-made composite scaffolds is still at least one order of magnitude lower than that of cancellous or cortical bone. The present challenge in tissue engineering is to design and fabricate bioactive and better mechanical properties for their specific application. In addition, more vivo studies are inevitable and the need for more studies in biological systems is imperative.

**References**

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History of Polymer Processing

by Thomas J. Wilde

To understand the history of polymer processing techniques it is first important to realize that naturally occurring polymers were manufactured and processes long before the invention of synthetic polymers. Horse and cow hoofs, animal horn, and tortoiseshell, were the main sources of the earliest plastic processing. These substances can be plasticized in boiling water and pressed or heated against a mold. Machines were already being developed that use the process of compression molding and thermoforming in the early 18th century to make products such as combs and buttons. Imported natural rubber was perhaps one of the most important products of the time. Edwin Chaffee patented the first calendering machine in 1833 and started the Roxburry India Rubber Company. The Calender processed rubber to make various clothing products and life vests. After Charles Goodyear patented the vulcanization process of Rubber in 1844, the product could withstand more extreme temperatures. Before this, rubber would become brittle during the winter. Gutta-percha is a naturally occurring gum found in trees in Southeast Asia had excellent insulating properties which were advantageous to the development of the telegraph industry. Shellac, a derivative from beetles, was a polymer with good wear resistance and strength produced for everyday appliances such as hand held mirrors or picture holders; even dentures were made from the polymer [1].

The progress of polymer processing goes hand in hand with the innovations in polymers themselves. This stemmed from the desire to abandon the limited supply of natural polymers and excelled through the realization of the potential of polymers as innovations continued to be made. The subsequent sections of this chapter attempt to describe the development of the modern processes chronologically to show the relevance of innovations developed. The advancements in injection molding and extrusion are given the most detail as these are arguably the most evolitional processes to the plastics industry.
1.1 Molding

Molding is the process of introducing a material into a cavity in order to manufacture the material into a desired shape. This technique of shaping a material dates back to the 3rd millennium BC when Mesopotamians manufactured metal shapes by pouring molten metal into a mold [2]. They created what is now the oldest existing cast of a copper frog [3]. After the first discoveries of polymers, methods were soon developed to mold polymers into desired shapes especially as the industrial revolution took off in the 19th century.

Molding was the first process for shaping plastic and is still today arguably the most used and important polymer processing technique. It allows for the shaping of complex, three dimensional designs which cannot be produced by other processing techniques. Many subcategories have developed within molding including injection molding and compression molding as well as many other techniques that are similar to these [4,5].

1.1.1 Injection Molding

In injection molding, the polymer is plasticized in a chamber outside of the mold from where it is forced into the mold. After cooling or curing in the case of thermosets, the part is ejected from the mold. The two mechanisms for forcing the polymer into the mold in today’s machines include a piston ram and a reciprocating screw [6] although the vast majority of injection-molding machines use a reciprocating screw. The main components of the injection molding machine are depicted in Figure 1. Plastic pellets or powder is fed into the hoper which is then transported to the mold via the screw mechanism.

![Figure 1. The Mechanism of the Injection Molding Machine](image-url)
The first ever injection molding machine was developed by J. W. Hyatt in 1872. This came after the development of “Parkesine”, known as the first man-made commercial plastic made from cellulose nitrate and produced by Alexander Parkes in 1861. Despite winning a medal for his creation at the 1862 International Exhibition in London, Parkesine didn’t take off like its creator wanted it to due to poor quality and high price [7]. Hyatt wanted to improve on the cellulose nitrate product that Parkes had begun when a billiard company, Phelan and Collander, offered $10,000 for an ivory substitute for billiard balls [8]. Hyatt was successful by combining the cellulose nitrate with camphor to produce a more stable polymer he termed Celluloid [9]. Celluloid would prove to be a successful product not only for billiard balls but for the mass production of hair combs, buttons, and photographic film [10]. The injection molding machine that Hyatt patented was much simpler than those of today but started the principles of a plunger used to inject the Celluloid through a heated cylinder and into a mold [11]. A man named E.L. Gaylord from England patented the actual process of injection molding in 1904 which his company used to make amber. The company fell out however due to the high cost of the amber products [12].

The importance of the injection molding machine cannot be understated when an inventor by the name of Leo Hendrick Baekeland began experimenting with phenol and formaldehyde in 1907. The development of electricity at the turn of the century required the use of insulating polymers. The current standard was the use of shellac, a natural polymer derived for the excretion of lac beetles. The natural polymer was very expensive and impractical for a growing electrical industry. Baekeland set out to replace shellac and in 1909 he introduced the world’s first purely synthetic polymer he coined Bakelite. The thermosetting polymer was not only a success in the electrical industry but it revolutionized the manufacturing industry by the seemingly endless amount of applications that Bakelite presented. His slogan was even “The Material of a Thousand Uses.” [13] The product was used for radios, machine guns, telephones, electric guitars, door knobs and many other appliances [14] throughout the first half of the 20th century. The more demand for products made out of plastic drove scientist and inventors to improve upon the current processing techniques.

The first true machine was developed by H. Buckholz in Germany in 1921. The Grotelite Company was given the license to manufacture the machine. The main drawback to this machine was that it was hand-operated. Development continued in 1926 in Germany as the company Eckert and Ziegler began mass-producing their own pneumatically operated
injection molding machines. The final instrumental advance to the plunger operated injection molding machine came in 1932 when H. Gastrow developed a method to enhance the heating and mixing in the heating chamber. He placed what is known as a “torpedo” in the center of the heating zone forcing the flow of polymer to the perimeter of the machine resulting in a better distribution of heat [12]. The biggest boom in the development of injection molding was yet to come however, until Americans needed plastic more than ever as they entered the World War II.

Lesser known to the Manhattan Project, and arguably just as important to the war was the Synthetic Rubber Project. Before the war, the United States acquired 97 percent of its rubber from Asian imports. After the bombings of Pearl Harbor, the United States effectively had no source of rubber which would be a crucial factor for soldiers considering they needed it for shoes, life vests, vehicle tires, tanks, gas masks, life rafts, and many other supplies [15]. According to the American Chemical Society, a military airplane used half a ton of rubber, a tank needed one ton, and a battle ship, 75 tons [16]. In 1946, the first screw injection molding machine was built by James Hendry. The advantage of the screw design was that it greatly enhanced mixing in the heating chamber of the machine. This allowed additives to be combined with the polymer such as colorants and recycled materials. Another advantage was the reduction in energy required to plasticize the polymer due to the addition of friction by the screw producing heat from inside. Once the polymer is gathered at the end of the screw, the entire screw acts as a plunger and rams the polymer into the mold [17]. The next advance to this design was W.H. Willert’s design of the reciprocating screw in 1952 in the United States. Previous designs for a reciprocating screw were seen during the war by H.P.M Queillery in France in 1939, as well as H. Beck in 1943 in Germany. This was a more cyclic process in which the screw moved backwards as the polymer melt progressed through the screw. The screw would then ram forward after enough polymer plasticized [18]. The reciprocating screw design accounts for 99% of injection molding machines today and has been fundamentally unchanged [4]. Advancements to this model have been made for more control and precision depending on the type of polymer used and the intricacy of the mold. Machines come in different shapes and models, and while most are horizontally oriented, some are vertically aligned for a very high level of precision is required. Many other innovations are simply the use of other machines around the injection molding machine that have taken the place of humans such as removal of parts, drying, transportation, and more.
1.1.2 Compression Molding

In compression molding a prepared amount of polymer or powder is placed over a mold and then pressed into the mold under high pressure and temperature for the polymer to fill the mold completely.

Since the discovery of natural plastics, the main mechanism for shaping them into designs was by compression molding or thermoforming. Samuel Peck is the first known molder in the United States beginning his work with shellac in 1852. He patented the photographic picture case in 1842. Alfred P. Critchlow manufactured horn buttons in England before immigrating to the United States and started the Florence Manufacturing Company [1]. Many of the products manufactured included jewelry, mirror backs, and game pieces such as dominoes, checkers, and billiard balls. The Charles Burroughs Company worked with J.W. Hyatt when he was first developing Celluloid providing him with hydraulic presses and molds. Early compression molding was a simple process in comparison to the large apparatuses that were being constructed for injection molding. The Charles Burroughs Company continued to pioneer the industry into the early 1900s with advances such as the tilting-head press and the hydraulic press. Other companies began to develop their own advances including the Shaw Insulator Company with air operated valves in 1946, semiautomatic with built in heat source by Western Electric Company in 1927, and optimization techniques of multiple presses operated by one person by General Electric in 1938 are important examples [1]. Compression molding continues to be a staple of the plastics industry today.

1.1.3 Transfer Molding

Transfer molding is essentially a progression of compression molding. However, instead of compressing a polymer directly into a mold, a polymer is compressed into multiple runners which lead to connect molds. This is particularly useful for similar parts of varying sizes and complex shapes such as electrical components [6].

Transfer molding was invented in 1926 by Louis Shaw at the Shaw Insulator Company when he needed to make intricate parts with multiple hollowed sections. One of the important products that came from this was the M-52 mortar fuse developed for soldiers in World War II and the need for so many informed many molders of the capabilities of transfer molding. Western electric developed a more sophisticated and economic machine which incorporated a dielectric heater to enhance the transferring of resin. James D. McDonald developed the first automatic transfer-molding machine in 1935. In 1946, Rockford Machine Tool designed an electric, fully automatic preheat transfer press. Marlin and Clyde Keaton included a screw
plasticizer as the mechanism to plasticize and transfer polymer through the runner tubes making the process similar to injection molding in 1949. George Scherry, an electrical engineer of Grayhill Moldtronics Inc., designed the transfer press for the company in response to a higher demand of parts for electronics. The result was a smaller machine. This allowed the manufacture of many of these machines to be run at once for mass production. In the following years, the reciprocating screw was adapted for transfer presses and optimized for the use of thermosets [1].

1.1.4 Thermoforming

Thermoforming has always been a method of molding naturally occurring polymers. It involves heating and applying pressure to a thermoplastic film or sheet over a mold, allowing it to soften and fill the mold. This process was used early on to make combs. The use of the method to make the black sharp key wrappings on wooden made pianos inspired E. Bowman Straton, a member of the Army Map Service, to use this same method to produce three dimensional maps in 1947. In 1938, Clauss B. Strauch built the first automatic thermoforming machine he coined the “Strauch machine”. Kraft Foods took advantage of the method to produce vinyl packages. During World War II, thermoforming was used to make windows of aircraft made of Plexiglas acrylic resin. Dr. Donald S. Frederick applied thermoforming to methyl methacrylate to manufacture large structural components of military aircraft and received the Hyatt Award in 1942 for his work. Thermoforming machines expanded to a variety of models depend on the specific applications they were being used for in the years following [1].

1.2 Extrusion

Extrusion is a processing method in which polymers are plasticized and forced through a die to produce a desired shape. Many finishing processes may occur after the extrusion process to make a finished part. Extrusion is responsible for producing the largest volume of plastics due to the fact that it can continuously cast. This is advantageous for producing long products such as tubing and pipes as well as sheets and film.

The first account of the present day extrusion technique occurred in 1797 when Joseph Brama made a ram-type device for making lead pipes. As the invention of the telegraph became more sophisticated and the idea of long distance communication fathomed, the need for insulating the wires grew. Thus, the extrusion process for polymers began in 1845 by H. Bewly
and R. Brooman for the cable making industry when machines were built for rubber and other natural polymers. The first insulated wire in the United States was then laid across the Hudson river in 1849 [19] followed by thousands of miles of insulated cable across the country. The extrusion machines produced by the cable industry were a ram type press which forced polymer through a die as copper wire was drawn [1]. The obvious disadvantage to this machine was that it was cyclic and thus cumbersome for producing very long wires. A.G. DeWolfe invented the first screw extruder for polymers in 1860 as a solution to this cyclic characteristic of the ram type extruder [20]. Many others produced publications of a screw extruder or made claims they developed the machine between the 1860’s and 1880’s however, Mathew Gray of England obtained the patent for the device in England in 1879. In the following year, other designs emerged from F. Shaw as well as in the U.K and John Royle in the United States. Paul Pfleiderer developed the first counter-rotating nonintermeshing twin screw extruder just one year after that in 1881. Gear pumps were included in the design of the extruder and patented by Willoughby Smith in 1887 [18]. A corotating intermeshing twin extruder was developed by R.W. Easton in 1916 which allowed for the mixing of polymers prior to movement through the die.

As synthetic polymers developed in the next few decades, extrusion was a difficult and often unsuccessful process for the rubber producers. It was evident that many factors played a role in the process, namely the length of the screw, temperature of the equipment, and the lower viscosity of the synthetic polymers. The chemical company DuPont, examined the science of extrusion by experimenting with various polymers and established many observations and guidelines which paved the way for design of thermoplastic extruders [1]. In 1935 Paul Troester produced the first extruder designed specifically for thermoplastics [21]. Friederich Krupp introduced a machine in 1941 he coined the “Knetwolf” which featured twin rotor mixing for masticating synthetic rubber (screw extrusion science and tech). Paul Leistritz’s company in Germany began to enhance the kneading and mixing process for the processing of tougher materials in the late 1930s and by the early 1940s had a design for extruding polyvinyl chloride [22]. In 1945, H. List of Switzerland developed the kokneter (Co-Kneader in English) which was a design of twin screws that slightly oscillated to wipe off built up polymer on the screws.

After World War 2 the realization of the potential that thermoplastics could have on society set in with many scientists. Companies both in the United States and in Europe started developing the modern science that describes the extrusion process today through experimentation and research papers. The 1950s and 1960s saw several new
designs and innovations being made to both the single and twin screw extruders. In 1953 the ZSK was developed by R. Erdmenger, G. Fahr, and H. Ocker which tweaked the features of the kokneter. Ferrel Corporation began designing machines in the 1960s that had separate screw and mixing rotor sections that proved very useful for thermoplastics despite being intended specifically for rubber [20].

The latest advances in extrusion technology come from the development of computers which allow engineers to control temperature, flow rate and torque. With the development of finite element analysis (FEA), the process can be well simulated before manufacturing to ensure the most optimal production.

1.3 Blow Molding

The idea of blow molding of plastic is rooted from glass blowing which had already become as sophisticated manufacturing technique during the time of the Roman Empire. Blow molding of polymers, however, is an additional process to either extrusion or injection molding. In extrusion blow molding, a preform is first extruded then clamped by a large mold which has a large diameter than the polymer. A blow pin is inserted through the polymer, and forces the expansion of the polymer to fill the mold. Injection blow molding begins with the injection molding procedure except with the use of a parison mold which allows for a hollow part to be formed. This part is transferred into a larger blow mold which then allows the blow pin to expand the part to fill the mold [6].

The technique of blowing the polymer into a mold developed after Hyatt invented Celluloid for many consumer products such as hair brushes, ping pong balls, jewelry and many others. The celluloid was first fabricated into thin sheets before being blown into the mold. The first blow molding device was created by Enoch. T. Ferngren and William Kopitke who sold it in 1937 to the Hartford Empire Company. Another company, the Plax Corporation, started up in pursuit of blow molding products. They began blow molding Christmas ornaments in 1940. Dr. Jules Montier invented anti-persperant in 1941 and teamed up with Plax Corporation in 1947 to make a bottle to house the product that could be squeezed to spay out the antiperspirant. His “Stoppette” bottle was the first mass produced plastic bottle and the idea of using plastic as a replacement for glass bottles had begun [23,24].

During World War II, the Owens Illinois Glass company began producing styrene canteens and bottles via the injection blow molding process. This method wasn’t practical for mass consumer production
however, because it left a plastic taste in the water. After the war, low density polyethylene became commercially available which made possible Montier’s Stoppettes but the material wasn’t satisfactory for bigger bottles. The availability of high density polyethylene in 1957 allowed for bigger, more stable bottles and a need for more robust processing methods.

The systematic design for injection blow molding evolved from four different processes. The first process was developed by A. Piotrawsky, who involved a vertical rotor parison mold. The mold would be filled on one side by the injection molding machine and then would rotate and insert the parison mold into a blow mold. The blow mold would then be ejected. The Moslo method utilized a vertical transportation of the parison mold from the injection mold to the blow mold. The disadvantages of these processes where that they didn’t have optimal ejection methods for the product. The Farkus method added additional horizontal movement after the vertical displacement for proper ejection of the material however it wasn’t very time efficient. The Guissoni method employs a three-stage rotation device in which the injection mold, blow mold, and ejection all occur simultaneously in a continuous process [4,23]. This is the method that is still in use today.

1.4 Rotational Molding

Rotational molding is a process that has existed since the time of ancient Egyptians who created ceramics and was a technique the Swiss used to make chocolate eggs. Rotational molding accounts for storage takes, trash cans, and footballs, luggage, ice chests and many other hallow applications.

Early plastics that were rotationally molded used a simple method of pouring a polymer into a very hot mold. When a thin layer began to solidify, the excess polymer was poured out. This method was used for some toys, doll parts, gloves and other products. In 1855, R. Peters in the U.K. patented the first method of biaxial rotation and heating for manufacturing hollow materials. This idea wouldn’t take effect in the plastics industry until a century later. Rotational molding didn’t start to take its current form until 1958 after low-density polyethylene became available. The McNeil Corporation is credited for the modern development of rotational molding when they began rotating molds about two axes in a large oven [1].

The ability to expand upon existing technologies requires the understanding of the history and current developments of that technology.
Polymer scientists of the early 1900s realized this and through competition and cooperation, were able to develop the manufacturing processes and sciences of polymers that exist today. The development of the Society of Plastics Engineers in 1942 was one of the great milestones that helped inform scientists what innovations had already been made and were in the process by other scientists. This collaborative effort, no doubt, paved the way to the machines that are built today.

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Extrusion
by Mengguo Yan

Extrusion is widely used in industry, not only in polymer producing, but also in metal, clay, ceramic manufacture or even food processing. However, in this chapter, only polymer, or plastic extrusion is focused.

The whole chapter contains four sections. The first section is background, which briefly and generally introduces the history of extrusion. Then, two of the most common types of extrusion, single and twin screw extrusion, cover the second and third section. The last section selectively states some of the latest application of extrusion technique.

12.1 Background

The first patent on extrusion can be dated back to the year 1797. But not until the decade of 1930, appeared the first industrial application. Since then, extrusions have been modified in different ways and become one of the most popular tools in various industries. Up till now, half of all plastic products, such as plastic bags, sheets and pipes, are made by this process. Moreover, extrusions have great use in the industry of foaming, pipe tubing, coating or even pharmaceutical industry. [1, 2]

Extrusion is a process to produce product by forcing raw materials through a die under certain controlled conditions, such as temperature, pressure, mixing and feeding rate. [2, 3]

Polymer extrusion process contains three basic stages. [4]

Stage 1. Melting solid polymer
Stage 2. Shaping molten polymer
Stage 3. Setting product shape and cooling down

In stage 1, polymer has a phase transition from crystalline solid into a liquid. In the meantime, the liquid is being transported forward until reaching the die. During stage 1, polymer melts should reach a uniform temperature and pressure for the next stage. [5] In stage 2, extrudate exit the die which controls the shape for a desired cross section. In stage 3, final product is shaped and cooled down.
Extruders in polymer industry have many different designs, which can be classified as followed. [6]

<table>
<thead>
<tr>
<th>Table 12-1. Classification of Polymer Extruders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw Extruders (Continuous)</td>
</tr>
<tr>
<td>Disk or Drum Extruders (Continuous)</td>
</tr>
<tr>
<td>Reciprocating Extruders (Discontinuous)</td>
</tr>
<tr>
<td>Single Screw Extruders</td>
</tr>
<tr>
<td>Multi Screw Extruders</td>
</tr>
<tr>
<td>Viscous Drag Type Extruders</td>
</tr>
<tr>
<td>Elastic Melt Extruders</td>
</tr>
<tr>
<td>Ram Extruders</td>
</tr>
<tr>
<td>Reciprocating Screw Extruders</td>
</tr>
</tbody>
</table>

Among the six types showed above, single screw extruders and multi screw extruders are the most common types and will only be described below.

### 12.2 Single Screw Extrusion

Single screw extrusion is considered as the most important type of extruder in polymer industry, since it is relatively lower-cost, easier designed and more durable. [5]

The motion of material in single screw extruder is straightforward. From the feed hopper, raw material enters and flows by gravity into extruder barrel. As raw material falls, friction between materials and screw surface and barrel is produced. It is the friction that pushes material to transport forward. While moving forwards, raw material is heated up and melted. As melted polymer reaches the die, its shape is adopted.

#### 12.2.1 Equipment

Single screw extruder contains five main components.

1) Drive system
2) Feed system
3) Screw, barrel and heater system
4) Head and die assembly
5) Control system

Components in a single screw extruder in detail are shown below in Figure 12.1. Drive system is constituted by motor, thrust bearing assembly and gear box, which is in charge of the motion inside the equipment. Feed system is made up of feed hopper, feed throat, and screw feed section. The main part of the equipment is screw, barrel and heater system, in which raw material is transported, heated, melted, mixed and pumped to the die. Among these three parts, screw is the heart and is introduced later in this section. Melt polymer leaves the extruder after through the die, where
product is shaped. Lastly, control system is responsible for the inputs and outputs, such as temperature and rev control.

Screw

Among all the components, screw can be regarded as the most important and worthy studied component in the whole system. A better designed screw is able to improve the production rate by 30-50%. [5]

The size of a conventional single screw can be described by its length and diameter and the ratio of length-to-diameter (L/D) is an important factor for single screw. Even with the same diameter, extruders with different L/D ratio have different throughput.

Longer extruders (higher L/D) have more melting and mixing capacity so that extruders can be allowed. Moreover, higher die pressure, less sharing heating with higher melting capacity and higher conductive heating from barrel can be reached.

Shorter extruders (lower L/D) have advantages as well. Less space is needed so that lower initial investment is requested. Also, lower replacement cost for screws and barrels. When processing temperature sensitive materials, residence time is less. Less torque and horsepower are needed as well.

The standard commercial extruders in the United States have D= 1.5, 2.5, 3.5, 4.5, 6, 8, 10, 12, or 14 inches and L/D= about 24, 30, or 36.

Even though screws have different sizes, there are three basic functions performed by the screw: 1) solid conveying function, 2) melting function, and 3) metering function or pumping function. Also, some other secondary functions are performed, such as distributive mixing, dispersive mixing, and shear refining or homogenization.

The simplest form of single screw extruders comes to “single stage” screw as shown in Figure 12.1. For this form, there are three sections separated as “feed section”, “transition section”, and “metering section” shown in Figure 12.2. The first section locates at the end of hopper with a constant and deep channel depth. Material in this section mostly remains in...
solid. The second section is also known as “compression section” which connects the “feed section” and “metering section”. A decrease in channel depth is made to cause compression of material in screw channel, which is essential to the proper functioning of the extruder. The last section is “metering section”, in which melted plastic is pumped forward until it reaches the die.

Figure 12.2 Geometric features of a single screw

12.2.2 Plastic Behavior
Plastics have different behaviors in different extruder zones. Unmelted solid plastic flows from feed hopper through feed throat and reaches extruder feed section by gravity. Then plastic is heated up and by the middle of screws’ “compression section” completely melted. Literally only melt polymer is conveyed forward through metering section to the die. However, in this chapter, only melt convey process is described.

Melt Conveying
Since the screw is not flat with different depth flights, melt polymer has a certain flow pathway in metering section. In a model of flows in metering section, it is assumed that the screw is stationary while the barrel is rotating. Below, Figure 12.3 shows the polymer flow path in the metering channel.

Figure 12.3 Melt conveying model.

According to this model, there are three kinds of flows considered. One is drag flow, created by the rotation of screw. Flow velocity near barrel wall is high and decreases to zero at the surface of screw. One other flow is pressure flow, which is produced by the high pressure from die and causes the melt polymer to flow back towards feed throat. It is similar to the plug flow in a pipe, which has a zero velocity at the wall and maximum in the center of the pipe. The last kind of flow is leakage flow, which is always
ignored. Unless the flight to barrel depth is larger than normal. The figure below shows the velocity profile in metering section.

Figure 12.4 Velocity profile in metering section

Generally, in the channel, melt polymer travels the fastest due to the drag flow with out back mixing. Back mixing caused by pressure flow occurs only in the area from screw to one third of the channel depth. Summarily, the extruder output is given by Eq.12.1 below.

Plastic Output \( (Q) = Drag \ Flow \ (Q_D) – Pressure \ Flow \ (Q_P) – Leakage \ Flow \ (Q_L) \) 12.1

12.3 Twin Screw Extrusion

Generally speaking, twin screw extruder is a machine with two screws inside. The first such extruder used in polymer processing was developed in the year 1930’s. Different types of twin screw extruder have been modified and used since then.

Twin screw extruder has distinguished properties and, of course, its own advantages and disadvantages compared to single screw extruder, such as better feeding and conveying, shorter residence time and narrower residence time distribution.

Moreover, materials transport is a major difference between twin screw and single screw extruders. Drag-induced forces are the major driving forces for twin screw; friction drag in the solid conveying zone and viscous drag in the melting zone. However, in a twin screw extruder, a displacement type of transport is observed.

Also, velocity patterns in single and twin screw extruder are different. The latter has a more complicated pattern. The complex flow in twin screw extruder has several advantages, such as better mixing, better heat transfer and larger melting capacity. On the other hand, the disadvantage for twin screw is the difficulty to describe the patterns and, thus hard to predict the performance of products.
12.3.1 Equipment

Twin screw extruder has similar appearance to the single screw extruder. It also has five main components.

1) Drive system  
2) Feed system  
3) Screw, barrel and heater system  
4) Head and die assembly  
5) Control system

As shown in Figure 12.5 below.

![Figure 12.5 Twin Screw Extruder](image)

For twin screw extruder, screw system is more complicated than single screw extruder. There are three common types of twin screw extruder: 1) Intermeshing co-rotating; 2) Intermeshing counter-rotating; 3) Non-intermeshing counter-rotating.

![Figure 12.6 Intermeshing co-rotating twin screw](image)

A typical intermeshing co-rotating twin screw is shown above in Figure 12.6. Melt polymer in intermeshing co-rotating twin screw is not as easy as intermeshing counter-rotating one to move forward, since two opposite velocities are produced by the two screws. Pressure is easily built up when melt enters the intermeshing area. In order to avoid high pressure, lower speed should be applied in process.

![Figure 12.7 Intermeshing counter-rotating twin screw](image)

Figure 12.7 shows a typical intermeshing counter-rotating twin screw. It possesses a better conveying character than co-rotating twin screw. However, it developed even higher intermeshing pressure. Thus, a maximum operable screw speed is limited.
Non-intermeshing counter-rotating twin screw, shown in Figure 12.8, can be considered as an intermediate of single screw extruders and intermeshing twin screw extruders. It has better mixing than single screw extruder but not as good as intermeshing twin screws. However, uniform melt pressure and material supplies are less comparable than intermeshing twin screws.

### 12.3.3 Plastic Behavior

Plastic behavior in twin screw system is far more complicated than that in single behavior. However, to some extent, there are some similarities in these two systems, which is that melt polymer has distinct behaviors in different areas. In feed zone, plastic solid drops into feed throat by gravity and is conveyed forward. The output rate, no matter whether it is co-rotating or counter-rotating, is determined by the feeding rate but screw speed. After solid is conveyed to a certain zone, melting happens. According to the screw length, a screw can either have or not a preheating zone. Then the melts are sent forward until enter mixing zone. Die is the last stop for a melt polymer before it exits the system.

### 12.4 Extrusion Applications

Extruders are widely used not only in chemical engineering industry, but also in pharmacy. Besides the application discussed belowed, extrusion can still be applied to other process, such as compounding, reproducing and so on.

#### 12.4.1 Extrusion Foaming [5, 7]

Foam can be defined as a gaseous void surrounded by a much denser continuous matrix. It exists in nature, such as cellulosic wood and sponge-like marine organism.

Polymer extrusion foaming technique started to transfer from lab to industry in mid twentieth century. Polymer foams can be developed into many functions, such as cushioning, insulation, protection, impact absorbtion and thermo/chemical electrical.
Polymer foams can be classified in various ways. By nature, it can be flexible or rigid; by dimension, sheet or board; by weight, high or low density.

Different foaming methods are suitable to different polymers. For example, the technique introduced here, extrusion foaming is suitable to PS, PVC, PE, PP and PVOH. Of course, there are more than one technique that can produce polymer foams. Injection molding is for ABS, PPO and PC; while mechanical blending is for PU, UF and Elastmor.

For extrusion foaming, no matter it is single screw extruder or twin screw extruder, pressure should be kept to compress the gas locked in the melt. Thus, in single screw system, the gas is foamed in the metering section and in twin screw system, is produced in downstream. Gas is still compressed in dies. After melts exit the die, gas is allowed to expand by the reduced pressure.

It is chemical blowing agent that produce gas during the extrusion process. However, blowing agent should not decompose in the melt, which results the release of gas through feed throat.

Blowing agent has three types: solid, liquid and gas. Solid blowing agent is mixed before extrusion. At the decomposition temperature, which is set in the certain zone in screw system, blowing agent generates gases. Different blowing agent has different decomposition temperature and generate different gases, such as nitrogen, carbon monoxide, carbon dioxide, ammonia or even water. Table 12.1 below shows the decomposition temperature of blowing agent.

<table>
<thead>
<tr>
<th>Material</th>
<th>Decomposition Temperature, °F (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celogen TSH</td>
<td>230–260 (110–120)</td>
</tr>
<tr>
<td>Celogen OT</td>
<td>316–320 (158–160)</td>
</tr>
<tr>
<td>Celogen AZ</td>
<td>401–419 (205–215)</td>
</tr>
<tr>
<td>Celogen RA</td>
<td>442–456 (228–235)</td>
</tr>
<tr>
<td>Saf-loam R/C</td>
<td>248–330 (140–165)</td>
</tr>
<tr>
<td>Saf-loam FP</td>
<td>316–360 (158–183)</td>
</tr>
<tr>
<td>Saf-loam RPC</td>
<td>360–600 (182–316)</td>
</tr>
</tbody>
</table>

Table 12.1 Decomposition temperature of blowing agent

At present, microcellular foaming is under research, which is done by injecting carbon dioxide into the system. Moreover, some attempts focus on using supercritical liuid.
12.4.2 Pipe and Tubing Extrusion

Pipe and tubing extrusion is profile extrusion with dies designed to produce cross sections. Thus, product can be either flexible or rigid; either small or large in diameter.

The choice of extruders depends on the final product. For small tubing, single screw extruders are common. As the diameter of product increases, the diameter of screw also increases as well. When the product is rigid, such as PVC tubing or pipe, counter-rotating twin screw extruders are used.

A common pipe or tubing extruder is shown in Figure 12.9 below.

![Figure 12.9 Equipment schematic of pipe or tubing extrusion line](image)

12.4.3 Wire and cable coating [5]

Coating wire and cable with a polymer is accomplished via a crosshead extrusion process in constant rate.

The most common polymer used in wire and cable coating including polyethylene (PE), polyvinylchloride (PVC), polyamide (PA), polybutylene terephthalate, thermoplastic elastomers, ethylene propylene copolymers, polypropylene and fluoropolymers.

Wire coating is always done by single screw extruders. Extruders melt the plastic and deliver it to the die with constant temperature and pressure. Two different kinds of die are used in wire and cable coating, pressure die and tubing die. The main difference between the two is where to coat the wire. Wires will be coated inside the pressure die while outside the tubing die.

After exiting the die, the polymer coating is cooled in water through, where the water should be applied uniformly on all sides of the wire coating to prevent shrinkage around the wire. Also, there’s a diameter gauge, which measures the wire diameter. If the diameter is too large, speed up the puller or slow down the extruder screw.

![Figure 12.10 Equipment schematic of pipe or tubing extrusion line](image)
12.4.4 Application in pharmaceutical industry [2, 3]

Not only extrusion is used in traditional chemical industry, but also pharmaceutical industry. Despite the drawbacks, such as the high energy input for the shear forces and temperature, it is still said that several obvious advantages already observed.

First of all, by extrusion, dissolution rate is improved. Also, the physical properties of drug can be modified by use of different polymer or even the process engineering. By the help of extrusion, solid drugs can be dispersed without solvent.

Since polymer is the carrier of drugs, it plays an important role in the extrusion system. The selection of polymer mainly depends on the drug-polymer miscibility, polymer stability and function of final dosage form. Most common carrier polymers are: polyvinylpyrrolidone (PVP), and poly(lactide) (PLA), poly (glycolide) (PGA) and copolymer of lactide and glycolide, poly(lactide-co-glycolide) (PLGA).
References

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6. Chris Rauwendaal. Polymer Extrusion
Injection molding is one of the most commonly used processing techniques for molding heat-induced softened materials, including most thermoplastics, some thermosets and some elastomers, under high pressure conditions. It consists of materials into a mold cavity where they are shaped in the injection. With the development of this technology, injection molding is widely used for manufacturing varieties of parts, such as fibers, ceramics and powdered metals, with polymers as binders.

In this chapter, process steps and equipment relevant to injection molding are discussed, with emphasis on the advantages and drawbacks of this technique. Meanwhile, its applications and future trends are critically reviewed.

13.1 Introduction

Injection molding is a rapid and versatile manufacturing process for producing parts by injecting material into a mold. It is often used in the plastics industry to produce objects with different size and shape. Material for the part is fed into a heated barrel and forced into a closed mold under high pressure and temperature conditions. After it cools and hardens to the configuration of the cavity, the finished product will be ejected at the end of the manufacturing cycle.

Both thermoplastic and thermosetting polymers can be processed by injection molding. Thermoplastics are prevalent due to characteristics that they can be molded to give the desired shape. To be more specific, when they are heated, they will undergo a physical change and a transition to a viscous state which can be repeated many times. On the other hand, thermosets are not as safe as thermoplastic. A thermoset polymer solidifies following heat-induced cross-linking and this chemical modification is responsible for the hardness of the resulting product. However, if the thermosetting polymer is not ejected from the injection barrel, crosslinking may also occur causing the screw and check valves to seize which will damage the injection molding machine.
Injection molding is a relatively young technique, born in 1872 by American inventor John Wesley Hyatt and his brother Isaiah, with a real expansion in the 1940s associated with a huge demand for inexpensive, mass-produced products due to the Second World War. The improvement brought about by injection molding is placing the auger inside the cylinder and mixing the injection molding material before pushing forward and injecting the material into the mold, which allows colored plastic or recycled plastic to be added to the virgin material and mixed thoroughly before being injected. Today screw injection molding machines account for 95% of all injection machines companies. The industry has evolved over the years from producing combs and buttons to producing a variety of custom products for many industries including consumer, toys, packaging, automotive and construction.

![FIGURE 1](image.jpg)

**FIGURE 1**
External structure of injection molding machine

### 13.2 Processes and equipment

Injection molding machines generally consist of two parts: the injection unit and the clamping unit. Injection Molding machines are distinguished depending on the configuration of such units, horizontal, vertical or hybrid. Injection unit consists of a hopper that feeds a heated barrel for heating, mixing, compression and melting. Several heater bands which located along the barrel are able to set and maintain different temperatures. Screw-type in the barrel is the pressure-generating element. When moving forward, the screw performs like a plunger to exert the needed pressure. The reciprocating screw can plasticize the material more quickly and uniformly with its rotating motion, as shown in figure below. There is a trick that although the screw should be designed to fit the characteristics of the processing material, the metering screw is the popular one for the rear
section has a smaller diameter than the front one and the material could be forced to flow into a narrower space. Thanks to this design, this process is associated with an increased speed that generates frictional heat. The transition area, between the meter and feed zones, is the intermediate area of the screw.

Another part of injection molding is the clamping unit while the mold is the terminal element of the injection molding. From the graph below we can find that it is composed of two halves that combine to form a cavity of defined three dimension shape which could form the outer surfaces of the molded object. It also has the ability to design molds with several cavities to produce more than one unit. There is a moveable platen allowing the two halves to become closed mold or open mold. During the injection process the clamping unit keeps the mold closed and extra clamping force needed to prevent the mold opening.

![Internal structure of injection molding machine](image)

**FIGURE 2**

Internal structure of injection molding machine

13.2.1 Mold cooling

The mold temperature is controlled by the cooling system. In this process, water is often used as the circulating fluid. After the injection process ended, the melt object cools down and solidifies in the mold. When it becomes hardened, the pins located in the mobile half of the mold will eject the object. Since the mold has to be cooled, there is a heat exchange system called temperature control unit needed, aims at removing the heat generated from the molten object. The cooling process begins on the injection of the molten object immediately, but the cooling time refers to the time from the solidification to the ejection of the part. To acquire mechanical properties, the melt object must undergo a curing process. Shrinkage can occur inside the mold and the object will change its size in terms of the cavity image. Generally the shrinkage can be characterized by two broad classifications,
The shrinkage should be taken care because if the imbalance of the shrinkage exceeds the mechanical strength of the part, warpage will occur. The anisotropic shrinkage will result in residual stresses for injection-molded parts are too weak to overcome the structural strength. These stresses can contribute to the premature failure of the part or they can relax over a period of time. Therefore, in order to obtain a perfect production by injection molding, warpage and residual stresses must be avoided.

13.2.2 Warpage and residual stress

As described in chapter 13.2.1, warpage occurs when the imbalance of the shrinkage exceeds the mechanical strength of the part. Residual stress happens when the injection-molded parts are too weak to overcome the structure strength, which can ultimately contribute to the premature failure of the part.

The shrinkage is dependent on many different process settings, where thermal distributions through the part thickness and over part areas are some of the most important. When the melt flows in the cavity, the shrinkage is developed. Meanwhile, the flow-induced effects can be attributed to shear forces. A shear field is developed because of the variations in the velocity field. The shear field makes the molecules of samples oriented in the direction of the main strain direction. If the polymer would be kept in its molten state, this orientation is recovered. When the melt meets the mold
solidifies, the molecules will keep their orientation in the flow direction as well as their molecular elongation. Consequently, the layer has a tendency to shrink in the direction of orientation. The molecules in the center of the melt are insulated from the cold metal allowing them to relax from their stretched orientation. In this way, they will have more time to recover from the oriented state and have less frozen in orientation and will also have fewer tendencies to shrink. This gradient of oriented molecules causes the surface compressed while the core is in tension which results in a warpage effect. This shrinkage effect becomes more complex due to the variations of the cooling rate, the direction and the velocity of flow. The balance of the strains and their directions results in residual stress which in its turn can contribute to warpage.

Different are shrinkage refers to differences in packing pressure, mold temperature or thickness. As the cooling rate is constant, thinner regions solidify more quickly than thicker regions. At a higher pressure the thinner regions will result in lower shrinkage. Meanwhile, cooler area will extract heat from hotter area which will cause a lower shrinkage than the hotter area. Furthermore, warpage is affected by variations in the process settings other than changing the material and the mold design.

13.3 Advantages and disadvantages

As a method of creating plastic products, injection molding is attractive to manufacturers because of multiple advantages it provides over other plastic molding methods. Overall, injection molding is simpler, more reliable, more versatile and more efficient than most other types of molding.

Injection molding operates at very high pressure, which provides the advantage of a greater amount of detail in the design of the piece being molded including complex geometry. Meanwhile, when compared to other types of molding processes, injection molding is fast which allows for far more products to be generated from the same mold. In other words, injection molding is highly efficient. Highly automation is another benefit of injection molding. Thanks to this advantage, very little overhead will have to go into paying labor force in a plastic injection molding process for commonly only one operator can run injection molding machine. In addition, there are other advantages such as little to no finishing of parts, minimum scrap losses and repeatability within tolerances.

However, the injection molding process still has several disadvantages to other molding processes which need to be improved. Generally, this is not a preferred method of manufacturing for short production runs due to the cost of tooling and the cost of operation. Meanwhile, it needs very long time for
design and development of parts working well while many parts are not suited to the long process. Hopefully, some measures can be taken to minimize these shortcomings.

One shortcoming of injection molding is that the mold tends to be very expensive and modifications of the mold while the design of the part to be produced is common and cost-consuming. As an essential tool for numerical simulation of the injection molding process, Computer-Aided Engineering is properly used to minimize the amount of redesign and retooling. The process is simulated in a computational environment and mold alterations and process settings can be tested again and again by using numerical techniques before the actual production of the tool. Studies have shown that up to 50% of costs can be cut for mold modifications and up to 15% for cycle time when using numerical process simulation.

The energy-saving method of injection molding machine has been put forward by some scholars in order to lower energy consumption of plastic products and achieve good economic benefits. For instance, variable-frequency technology in saving energy of injection molding machines, variable-volume pump and servo control technology in saving energy of injection molding, energy accumulator in saving energy of injection molding machines, two-plate clamping device in saving energy of injection molding machines, all-electric driven or electro-hydraulic hybrid driven technology in energy saving of injection molding machines, are mainly representative research work in this field. By the development of this technology, injection molding tends to become a combination of mechanical and electrical control technology, which makes itself more efficient and environmentally friendly.

13.4 Applications

In our daily life, there are many things are created by injection molding, for instance, wire spools, packaging, bottle caps, pocket combs, some musical instruments (and parts of them), one-piece chairs and small tables, storage containers, mechanical parts (including gears), and most other plastic products available today. Also, injection molding is the most common modern method of part manufacturing which is ideal for producing high volumes of the same object.

Generally, injection molding is used for manufacturing plastic, rubber and metal. Materials are fed through a heated barrel in the machine and forced into a mold where it will cool and take its shape. An injection molding machine can stamp out metal car shell parts, rubber valve steam seals, and even plastic toys for kids.
13.4.1 Plastic injection molding

Plastic injection molding is the most widely used production technology in plastic industry, which contains a variety of high-tech products, auto parts and generic household products. It not only can improve productivity but reduce plastic material loss. In addition, it can be used to mold complex articles and offer high dimension precision. Taking the development of toys as an example, about 80% of the total quantity of toy parts is made up by plastic injection molding while the rest are largely standardized parts as screws.\(^\text{16}\)

Plastic molding is ideal for producing high volumes of the same object. The advantages of using plastic materials are that they are lightweight and relatively low cost, while having good mechanical properties. In addition, the primary processing techniques for polymer materials such as extrusion and injection molding are continuing to evolve to keep pace with other advances in related fields. One major reason injection molding is a popular method of manufacturing is its ability to produce plastic parts rapidly with intricate shapes within very tight specifications.

13.4.2 Rubber injection molding

Rubber injection molding is a manufacturing process used to create rubber parts as rubber automobile parts and rubber hoses. It is ideal for creating small parts which require precision to fit inside other components. Rubber parts are widely used in a range of mechanical parts and machines. Commonly, the rubber injection molding can be found in a press shop or in the manufacturing sector.

The basic process used in rubber injection molding is quite simple. A mold is created out of metal with the exact specifications and dimensions of the rubber part. This mold is inserted into a press and connected to a rubber injection system. A press applies pressure to hold the top and bottom parts of the mold together. Rubber is injected into the mold using a large ram or screw. The heated, uncured rubber is forced into the mold cavity using an injection nozzle. Extra rubber or overflow may occur, due to the force required and the need to fill the mold completely. As the rubber cools, it separates from the walls of the mold, while retaining the details and shape of the design. The press opens and the rubber part is released. The rubber is heated and temperature controlled by the rubber injection press. The actual molds themselves are typically made of stainless steel and are not designed to retain heat. In fact, many designs require the mold to be quickly cooled, forcing the rubber to cure within a smaller time frame.
The entity of the rubber injection molding system presented in this chapter is shown in Fig. 4. The mold is heated using both upper and lower heating plates simultaneously to achieve a desired temperature. As shown in Fig. 4, the upper and lower plates are composed of six 220V, 1200W heaters connected in a triangular shape. The heating plates are driven by solid-state relay drivers and temperatures are measured by sensors.

With the development of rubber injection molding, the productivity of the system increases greatly and the reliance on human intervention reduces in the manufacturing process. It is known that rubber is a natural resource that is quite expensive to obtain and should not be wasted. Therefore, to maintain low cost and minimize waste in the process, reducing the amount of rubber lost is critical and essential.

### 13.4.3 Metal injection molding

Metal injection molding is well-established, cost-effective method of fabricating small and moderate size metal components. It can not only create automobile parts from spark plugs and floor pans to ball bearings, but also create items like TV hangers and knitting needles.

The metal injection molding can be divided into four steps, mixing, injection molding, debinding and sintering, respectively. In the process of metal injection molding, the metallic powders are injected into the mold. There is a difference between metal injection molding and other type of
Injection molding is the use of binder material, which is due to the plasticity and fluidity of the powder. All binder systems are based on two important major groups of ingredients, polymers and waxes with minor additions of lubricants, surfactants and coupling agents. At the mixing stage, both metal powder and the polymeric binder are combined into a homogeneous mixture. After injection molding, the binder is removed from the molded part, leaving behind the metal skeleton that retains the molded shape. The remaining brown part is then sintered at elevated temperatures and the metal powder particles will be bonded together and consequently this step provides the strength in the finished product.

**FIGURE 5**
Metal Injection Molding

### 13.5 Future trends

Nowadays, with the rapid development of injection molding, it becomes more and more versatile which can be used in a variety of fields such as cosmetic/pharmaceutical packaging. To be more specific, through the innovative co-injection technique, Vaz and co-authors proposed a bi-layer delivery system based on soy protein. This technique represents an evolution of traditional injection molding. Meanwhile, many innovative technologies of injection molding have been developed to overcome the limitations of conventional injection molding. Taking gas-assist injection molding as an example, it is now making inroads in the medical industry, offering new technical and creative possibilities to original equipment.
In fact, recently, traditional injection molding is replaced by a new technology known as powder injection molding, which is a net-shape fabrication technology that combines the complex shape-forming ability of plastic injection molding, the precision of die-casting and the material selection flexibility of powder metallurgy. As described in 13.4.3, this technology mixes a small amount of a polymer with inorganic powders to form a feedstock that can be injected into molding cavities. After that, the binder is extracted and the shaped part is sintered by injection molding.

As to the future of this technology, some scholars offered their suggestions and opinions. Dimov reported the survey results to help inform European research and industry about the current trends and applications requirements in the development of Micro- and Nano-manufacturing technologies and presented the key technologies which are essential to the future micro manufacturing for research communities and industries. Injection molding has been chosen to be the third important technology by the whole survey and recognized more important by the industries. It is considered as one of the most important future technology in powder metallurgy. Considering the Micro-manufacturing and Nano-manufacturing are the major trend in the future, the challenge for injection molding process will be targeted on how to create the micro feature sizes successfully.

Therefore, although it is not clear whether injection molding technology represents the future of the manufacturing market, it is still a promising approach which needs more exploration and research.
References

Joining (welding) of Polymers

by Tianyu Yu

14.1 Background

Polymers are progressively replacing metals in the automotive and aerospace industries over the past few decades. Polymeric materials are as strong as or even stronger than some metallic alloys, exhibiting improved mechanical performance, thermal insulation properties, chemical and corrosion resistance along with increased design freedom to manufactured products. On the other hand, polymers have become more mechanically reliable and also cheaper owing to the processing and fabrication advance supported by the fast development in industries [4] [11].

Joining/welding of polymers is an important step in manufacturing of aerospace thermoplastic composite structures. Joining of polymers can be categorized into mechanical fastening, adhesive bonding, solvent bonding, co-consolidation, and fusion bonding or welding [3]. The basic process of welding includes heating and melting the bond surface of polymer, pressing these surfaces together, following cooling solidification and consolidation. The strength and stability of the components welding layer are important in this process.

It is quite important to improve the welding layers or joints strength and stability under different circumstances such as high moisture and high temperature. The welding joints can deteriorate mechanical and thermal properties of polymer, but the size of a component is usually limited by its application or production process. Nowadays more and more polymer product need to be welded in order to design hybrid structures, therefore it is quite important to understand the mechanism of polymers joining/welding.
14.2  **Joining Techniques background**

More and more joining techniques have been developed for un-reinforced and reinforced polymer joining Fig.14.1 [14].

![Diagram of Joining Techniques]

Each of these techniques has its limitation. The mechanical fastening joining is labor and time consuming which means low efficiency and has problems such as stress concentrations, galvanic corrosion, mismatch of coefficient of thermal expansion, and damage of reinforcing fibers induced by drilling. It is not easy to bond adhesive materials to polymers in adhesive bonding [15]. Most of these drawbacks can be eliminated by polymer welding.
14.3 Welding Technique

Fig. 14.2 shows different types of fusion bonding, which mainly consists of thermal welding, friction welding and electromagnetic welding [3]. Fusion bonding normally consists of a surface process, heating the polymer interface, forcing polymer chains to inter-diffuse, and cooling.

14.3.1 Friction Welding

Friction welding is a generation of heat at a joint interface from frictional work under the application of pressure, followed by cooling and consolidation of the polymer. There are several kinds of friction welding such as linear vibration welding, spin welding, ultrasonic welding, and friction stir welding [3]. Normally, this friction is between a moving workpiece and a stationary component, with a lateral force to plastically displace and fuse the bond.

14.3.1.1 Vibration Welding

In vibration welding, two components are pressed into contact, one is fixed and the other one vibrate laterally under controlled frequency and amplitude.

When the total heat reaches a certain which can melt and mix the polymers, after fusion the polymers, the parts are aligned and consolidated under another pressure. Fig. 14.3 shows different kinds of vibration welding method.
Some of the advantages of this process are the following: (a) high process controllability and flexibility, (b) high production rates, (c) large parts capability and design freedom, (d) possibility of performing internal joints, hermetic seals, and entrapment of parts (e) low level of surface preparation, and (f) no fillers are required. And some limitations are: (a) flat surface shapes required to be welded, (b) vibration can cause damage of electronic components, (c) high level of noise due to vibration (90–95 dB), (d) expensive machinery, and (e) limited availability of joint geometries [17].

Vibration welding has found many applications in the automotive and domestic appliance industries. Automotive applications include front and rear light assemblies, fuel filler doors, spoilers, instrument panels, ductwork and reservoirs for brakes, power steering, and vacuum systems [17-18].

### 14.3.1.2 Spin Welding

Spin welding is also called “rotary friction welding,” usually the welding components are compressed and rotating, producing heat to melt. One requirement for spin welding is that the rotating surfaces must be symmetric.

Some key process parameters in this welding method are the rotational speed, the friction pressure, the forging pressure, axial displacement, and the welding duration. Rotational speed is normally within 9.1–15.2 m/s, and friction and forging pressures are within 80–150 kPa and 100–300 kPa, Welding times are usually at 2 s [16][19].

Some advantages of spin welding are the following [19]: (a) no additional filler material, (b) hermetic sealing, (c) energy efficiency, (d)
low level of emissions, and (e) low cost. The associated main disadvantages are the following [19]: (a) limited to symmetric geometries, (b) limited production rate, and (c) low geometric tolerance. Fig.14.4 shows a typical schematic of spin welding machine [20].

![Typical schematic of the spin welding machine](image)

**14.3.1.3 Ultrasonic Welding**

Ultrasonic waves are used to generate frictional heat on the welding polymers. Like the former two methods, ultrasonic welding also needs to press the two welding parts together, but use a vibrating horn this time.

The weldability is basically determined by base material stiffness. The greater the stiffness, the better the weldability will be, due to the improved ultrasonic vibration transmission [4].

Ultrasonic welding advantages are the same as spin welding. Its disadvantages are as follows: (a) sample size limitations (maximum of 0.23 m 3 0.3 m), (b) usually only for compatible thermoplastics, (c) noise concerns, and (d) expensive equipment. Other common problems in vibration welding, are the damage of electronic components. Applications of ultrasonic welding are in domestic appliances (white goods) and medical appliances. In automotive, instrument panels are joined with metallic pieces by means of metallic inserts [21].

**14.3.1.4 Friction Stir Welding**

Friction stir welding (FSW) is first developed for metallic alloy [22]. Then it is widely used in composite and polymer welding process. In FSW, the parts to be welded are placed firmly together. A head-pin of a rotating
metal tool drills and plunges into the parts at joint line till the tool shoulder sits on the top surface of the parts. Then rotating metal tool drives in the weld zone [3]. Fig. 14.5 [23] shows the schematic of the friction-stir welding process. The heat is produced by the metal tool shoulder and head pin rotating, the toll translates along the joint zone, stirring the melt polymer.

Some advantages of FSW are: (a) can be used to join dissimilar materials [24]. (b) higher assembly rates (c) reduce the stress concentrations by drilling holes. Some disadvantages of FSW are: (a) may need surface preparation before welding. (b) local damage by stirring or tool motion [4].

![Fig. 14.5](image)

**FIGURE 14.5**
Schematic view of the friction-stir welding process [23].

### 14.3.2 Thermal Welding

Thermal welding consists of an external heating stage and a forging stage. An external heat source applies heat directly to the individual bonding surfaces to melt the matrix. The heat source is removed and bonding surfaces are brought in contact under the forging pressure. Thermal welding can be divided into hot-tool (plate) welding, infrared welding, hot gas welding, extrusion welding, and laser welding [3].

#### 14.3.2.1 Hot-Tool Welding

Typically, the mechanism of hot-tool welding is that a heated plate is clamped between the surfaces to be welded to melt the interfaces. Then,
withdraw the hot-tool, press the polymers until they solidify, Fig 14.6 shows a schematic of hot tool welding [3].

Some major process parameters for hot-tool welding are thickness of molten material which is called the meltdown, welding penetration. The higher welding penetration is, the lower the weld strength for different meltdown thicknesses [25]. The main advantages of hot tool welding are as follows: (a) ease of assembly, (b) do not need filler (c) a big range of materials are weldable by hot tool, (d) shape freedom, (e) low emission levels, (g) high production rates, and (h) welding of large parts. The disadvantages are the following: (a) high energy consumption, (b) slow start-up (15–30 min) due to the warm-up of the tool (c) residual stress is large, (d) cleaning of accumulated residual plastic on the tool is required, and (e) expensive equipment [16].

The most common hot gas-welded materials are polypropylene (PP), polyethylene (PE), poly-vinyl-chloride (PVC), polycarbonate (PC), and polyamide (PA) [19].

14.3.2.2 Infrared Welding

Infrared welding is a non-contact welding technique which can be divided into three processing steps [26]: 1) infrared heating of the interface, 2) change-over, and 3) joining and cooling under pressure (Figure 14.7).
Infrared radiation usually produced by high-intensity quartz lamps. The important welding parameters are: heating time, change-over time, and forging pressure on polypropylene polymer butt-welded parts. It was shown that increasing the heating time enhances the weld strength until a critical value is reached. It is similar in welding pressure on weld strength for different welding times. By increasing the change-over time it increases the cooling time, which is reducing the thickness of the molten polymer film resulting in lower weld layer strength [26].

Some advantages for infrared welding are: (a) it can be used to join a combination of flat and curved parts. (b) easy assembly. (c) Process parameters can be controlled better. Main disadvantage is possible deconsolidation and warpage of substrates during the heating process [3].

14.3.2.3 Hot Gas Welding

As we all know, the most traditional metal welding is the oxy-acetylene gas welding, where we use a heating gas to melt the layer. Typically, two parts are placed in contact and filler is deposited in the joint. The gas melt the joint area, then two parts are pressed together to consolidate.

To ensure the strength of welding layer, it is needed to control the purity of gas, and the use of solvent cleaning or grinding of the joining surfaces is required prior to welding. Important process parameters are gas temperature, gas flow, and welding speed [27]. Fig 14.8 shows the schematic of hot gas welding technique.
The main advantages of hot gas welding are as follows [28]: (a) cheaper welding equipment (b) high grade of shape freedom for joining parts, (c) portable equipment, (d) great range of materials can joined, and (e) low skill operating level. The disadvantages of process are the following [28]: (a) low welding speeds, (b) use of filler material, and (c) manual operation.

14.3.2.4 Laser welding

Most researchers focus on Laser welding which is one kind of thermal welding recently.

Laser transmission welding has become more and more popular by displaying its specific advantages such as offering flexible seam contouring, minimal heat input, mechanical stress and consistent weld quality [6]. in establishing welding processes for thermoplastics. However, according to Becker, F. et al., there are no developed process variants so far, a physico-mathematical model considering the different energy conditions for joining parts with various absorption properties should be developed and they conducted experiment to collect data of temperature progression for polypropylene. They also built a FEA model to compare with experiment data [1].

Their results showed that the laser transmission welding of polypropylene by the contour method is based on the melting depth. Different energy conditions can be used to calculate the molten layer thickness of the two welding parts [1].

Laser transmission welding has its advantages when it comes about local deposition of energy and minimum thermal distortion in the joining components. Andrei Boglea et al. developed a new approach for the laser transmission welding developed for the packaging of disposable polymeric microfluidic-biochips. They used a fibre laser and a tailored method for the
laser energy deposition was tested on the sealing of polymeric biochips with a covering foil. This method combines the characteristics of the polymer contour welding and quasi-simultaneous welding and allows the achievement of contamination-free, high quality weld seams as narrow as 100 mm with a high dynamic which makes it also suitable for the high volume production. The weld seams width of their micro-welding of polymers with fibre lasers is around 100 µm which can meet the need of many new microfluidic devices. They also reduced the heat affected depth, their future work will focus on reducing the laser spot down to 30 µm [2].

Friedrich G. et al. used high power diode lasers in polymers welding. This high power diode lasers have advantages such as short process times, providing optically and qualitatively valuable weld seams, contactless yielding of the joining energy, absence of process induced vibrations, imposing minimal thermal stress and avoiding particle generation [5].

Giuseppe Casalino et al. developed a model for thermo-morphologic and mechanical behaviour of thermoplastic polymers during the laser welding. They analyzed Keyhole and conduction welding for butt and overlap configurations [6]. A.S Wood built a butt-fusion welding of polymers model based on the definition of an enthalpy function which is constructed for the evolutionary heat transfer [7]. A contact-free method infrared thermography is used for surface temperature measurement by Maryna Speka et al, by collecting the data with a numerical simulation of the temperature field evolution inside the components, an assessment of optimal process parameters is possible [8]. Mariana Llie et al. built models based on Mie theory to describe the laser beam behavior in semi-transparent media and to approximate the laser power distribution at the interface. They can also be used to predict the temperature field in both parts [9]. Xiaochu Wang et al. expose heterogeneous polymer materials to a high-pressure fluid. This fluid promotes interpenetration and also increases chain mobility at the interface. They investigate the effect of the high compressibility of supercritical (SC) fluid on the compatibilization of two incompatible polymers [10]. Fig 14.9 [3] shows the schematic of laser transmission welding technique.
The main advantage of using laser radiation in metalworking is the ability to provide a highly concentrated energy over a very small area. Another one is the process is very fast. Main disadvantage is the high cost [3].

**14.3.3 Electromagnetic Welding**

Electromagnetic welding consists of molding opaque powders or inserts such as iron oxide, stainless steel, ceramic, ferrite, and graphite, into the polymer matrix between the parts to be joined. A high-frequency magnetic field causes the magnetic materials at the weld interface get hot and start melting the surrounding polymer. Types of electromagnetic welding techniques include induction welding, dielectric welding, microwave welding, and resistance welding [3][13].

**14.3.3.1 Induction Welding**

In induction welding, there is usually an implant or susceptor positioned in a high- (radio-) frequency electromagnetic field in the range of 200–500 kHz. The implant can be ferromagnetic materials in the form of foil-like tape or micron-sized particles molded in polymer. The melting heat comes from the eddy currents induced by an electromagnetic coil [3]. Fig.14.10 shows the mechanism of induction welding.
Induction welding generally consists of a power supply or generator, in which an induction coil can transmit the magnetic field to the weld layer, a placement nest and an implant [29].

The main process advantages are the following [16]: (a) high production rates, (b) high strength welding layer (c) entrapment of parts, (d) welding of similar and dissimilar materials, (e) hermetic seals, (f) large part capability, and (g) precise heating control. The disadvantages are [16]: (a) filler material is required (insert), (b) complicated assembly operations, (c) increased stress concentration (d) expensive machinery, (e) insert can corrode decreasing joint strength, and (f) electromagnetic field can cause extra heat on other parts.

### 14.3.3.2 Dielectric Welding

Dielectric welding is also called “Radio Frequency Welding”, Figure 14.11 shows the scheme of radio frequency welding.
FIGURE 14.11
Scheme representation of the radio frequency welding [4].

The technique relies on the heating associated with the dielectric hysteretic losses of the polar thermoplastics. Under high frequency alternate electric field, polar polymers have their dipoles reoriented according to field polarity, producing heat for welding [19]. Some advantage is short welding time, joint interface is not exposed to outside atmosphere. Main disadvantage is only materials with very high dielectric constants can be welded by using this method [4].

14.3.3.3 Microwave Welding

We are quite familiar with microwave because we use it every day. In microwave welding, a thin layer of electromagnetic absorbent material is placed between two parts. The microwave energy is usually in GHz which induces a temperature rise to melt the electromagnetic absorbent material [3]. Figure 14.12 shows the Schematic of the microwave welding.
Some advantages are: (a) saving energy, (b) low cost, (c) can produce internal joints, (d) clean to environment. Disadvantages are: (a) to use an absorbing insert material in joint, (b) limitation of the size of parts [3-4]. Microwave welding is a relative new technology and has potential applications in industry.

### 14.3.3.4 Resistance Welding

Resistance welding usually uses implant or electrical resistance, such as metal mesh and carbon strip in the welding layer. By applying an electrical current, it increases the temperature in resistance. Figure 14.13. shows the schematic of resistance welding process.
Resistance welding can be used in most polymers and has the advantages such as fast, cheap, easy to handle, clean, can be used in large structures [31]. Limitations are the following [21]: (a) the obligatory use of a resistance element, (b) long welding times, (c) limited recycling of the welded component due to the present implant, and (d) relative high operating skills are required.

14.4 Summary

Polymers are increasingly used in recent years, progressively replacing metals in industry because they are strong, light in weight, cheap, higher thermal and corrosion resistance. In order to better use polymer structures, more and more welding technique has been developed. In this chapter, three classes of welding/joining techniques are introduced, i.e., friction welding, thermal welding, and electromagnetic welding. Vibration welding can be used to weld small parts; Spin welding can be used to weld rotational symmetric parts; Ultrasonic welding is clean but need surfaces preparation; Hot gas welding is easy to operate; Laser welding is growing in importance because its fast, clean, smooth flash, low residual stresses and accurate. Microwave can be used in complex geometries but not suitable for conductive parts. Resistance welding is good for large flat surfaces welding. It has been shown that polymer welding/joining is a developing and promising technique can cover a wide range of applications and more research will be conducted on it.
References


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