

## 5. Introduction

Of the three basic types of materials, polymers are the newest and at the same time the oldest known to man. Polymers form the living organisms and vital processes of all life on Earth. To ancient man, biological polymers were the source of food, shelter, and many of his implements. However, our interest in this chapter is in polymers other than biological. With the exception of natural rubber, nearly all of the polymeric materials used in engineering today are synthetic. The materials themselves are made by chemical processing, and most of the products are made by solidification processes.

A **polymer** is a compound consisting of long-chain molecules, each molecule made up of repeating units connected together. There may be thousands, even millions of units in a single polymer molecule. The word is derived from the Greek words poly, meaning many, and meros (reduced to mer), meaning part. Most polymers are based on carbon and are therefore considered organic chemicals.

Polymers can be separated into plastics and rubbers. As engineering materials, they are relatively new compared to metals and ceramics, dating only from around the mid-1800s

For our purposes in covering polymers as a technical subject, it is appropriate to divide them into the following three categories, (1) Thermoplastic polymers, (2) Thermosetting polymers, (3) Elastomer.

1. **Thermoplastic polymers**, also called thermoplastics (TP), are solid materials at room temperature, but they become viscous liquids when heated to temperatures of only a few hundred degrees. This characteristic allows them to be easily and economically shaped into products. They can be subjected to this heating and cooling cycle repeatedly without significant degradation of the polymer.

2. **Thermosetting polymers, or thermosets (TS)**, cannot tolerate repeated heating cycles as thermoplastics can. When initially heated, they soften and flow for molding, but the elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid. If reheated, thermosetting polymers degrade and char rather than soften.

3. **Elastomers** are the rubbers. Elastomers (E) are polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape.

Although their properties are quite different from thermosets, they have a similar molecular structure that is different from the thermoplastics.

Thermoplastics are commercially the most important of the three types, constituting around 70% of the tonnage of all synthetic polymers produced. Thermosets and elastomers share the remaining 30% about evenly, with a slight edge for the former. Common TP polymers include polyethylene, polyvinylchloride, polypropylene, polystyrene, and nylon.

Examples of TS polymers are phenolics, epoxies, and certain polyesters. The most common example given for elastomers is natural (vulcanized) rubber; however, synthetic rubbers exceed the tonnage of natural rubber.

The growth in applications of synthetic polymers is truly impressive. On a volumetric basis, current annual usage of polymers exceeds that of metals. There are several reasons for the commercial and technological importance of polymers:

- i. Plastics can be formed by molding into intricate part geometries, usually with no further processing required. They are very compatible with net shape processing.
- ii. Plastics possess an attractive list of properties for many engineering applications where strength is not a factor: (1) low density relative to metals and ceramics; (2) good strength-to-weight ratios for certain (but not all) polymers; (3) high corrosion resistance; and (4) low electrical and thermal conductivity.
- iii. On a volumetric basis, polymers are cost-competitive with metals.
- iv. On a volumetric basis, polymers generally require less energy to produce than metals.
- v. This is generally true because the temperatures for working these materials are much lower than for metals.
- vi. Certain plastics are translucent and/or transparent, which makes them competitive with glass in some applications.
- vii. Polymers are widely used in composite materials

On the negative side, polymers in general have the following limitations: (1) strength is low relative to metals and ceramics; (2) modulus of elasticity or stiffness is also low—in the case of elastomers, of course, this may be a desirable characteristic; (3) service temperatures are limited to only a few hundred degrees because of the softening of thermoplastic polymers or degradation of thermosetting polymers and elastomers; (4) some polymers degrade when subjected to sunlight and other forms of radiation; and (5) plastics exhibit viscoelastic properties, which can be a distinct limitation in load bearing applications.

## 5.1 Fundamentals of Polymer Science and Technology

Polymers are synthesized by joining many small molecules together to form very large molecules, called macromolecules, that possess a chain-like structure. The small units, called monomers, are generally simple unsaturated organic molecules such as ethylene ( $C_2H_4$ ). The atoms in these molecules are held together by covalent bonds; and when joined to form the polymer, the same covalent bonding holds the links of the chain together. Thus, each large molecule is characterized by strong primary bonding. Synthesis of the polyethylene molecule is depicted in Figure 8.1. As we have described its structure here, polyethylene is a linear polymer; its mers form one long chain.

A mass of polymer material consists of many macromolecules; the analogy of a bowl of just-cooked spaghetti (without sauce) is sometimes used to visualize the relationship of the individual molecules to the bulk material. Entanglement among the long strands helps to hold the mass together, but atomic bonding is more significant. The bonding between macromolecules in the mass is due to van der Waals and other secondary bonding types.

Thus, the aggregate polymer material is held together by forces that are substantially weaker than the primary bonds holding the molecules together. This explains why plastics in general are not nearly as stiff and strong as metals or ceramics.

When a thermoplastic polymer is heated, it softens. The heat energy causes the macromolecules to become thermally agitated, exciting them to move relative to each other within the polymer mass (here, the wet spaghetti analogy loses its appeal). The material begins to behave like a viscous liquid, viscosity decreasing (fluidity increasing) with rising temperature.

### 5.1.1 Polymerization

As a chemical process, the synthesis of polymers can occur by either of two methods:

(1) addition polymerization and (2) step polymerization. Production of a given polymer is generally associated with one method or the other.

**Addition Polymerization:** In this process, exemplified by polyethylene, the double bonds between carbon atoms in the ethylene monomers are induced to open so that they join with other monomer molecules. The connections occur on both ends of the expanding macromolecule, developing long chains of repeating mers. Because of the way the molecules are formed, the process is also known as chain polymerization. It is initiated using a chemical catalyst (called an initiator) to open the carbon double bond in some of the monomers.

These monomers, which are now highly reactive because of their unpaired electrons, then capture other monomers to begin forming chains that are reactive. The chains propagate by capturing still other monomers, one at a time, until large molecules have been produced and the reaction is terminated. The entire polymerization reaction takes only seconds for any given macromolecule. However, in the industrial process, it may take many minutes or even hours to complete the polymerization of a given batch, since all of the chain reactions do not occur simultaneously in the mixture.

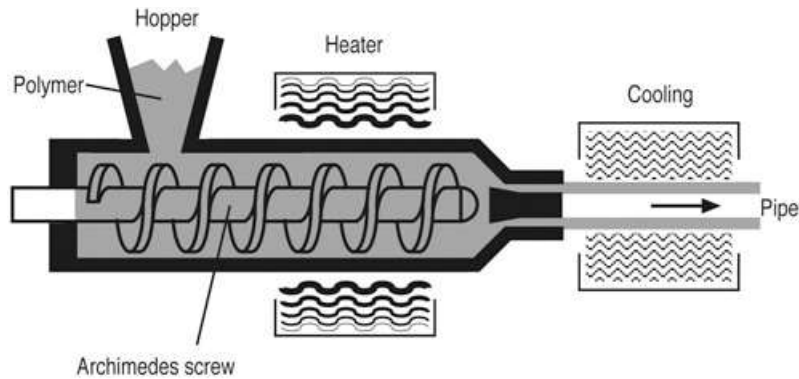
## 5.2 Plastics Processing

Because of the properties of polymers it is possible to mould them and change their shape using a number of different repetitious manufacturing processes.

The most important of these are extrusion, injection moulding, blow moulding, vacuum forming, extrusion blow moulding, rotational moulding, calendaring, foaming and compression moulding.

### Extrusion

Extrusion is a process that can be compared to squeezing toothpaste out of a tube. Thermoplastic granules are forced through a heated barrel and the fused polymer is then squeezed through a die that is the profile of the extruded component.



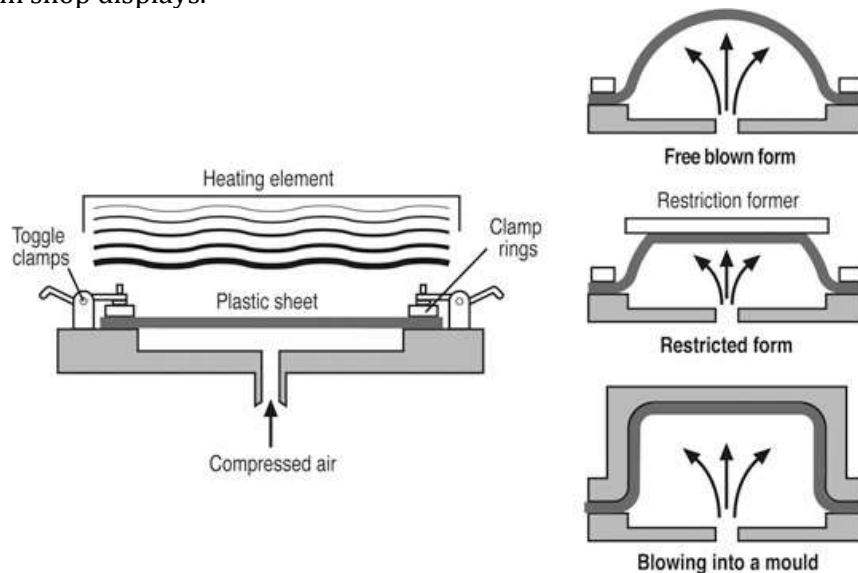
### Extruding a pipe

The extrusion is cooled by water or air as it leaves the die and is finally cut to the required length. The shape of the die can be varied from a simple hole with a centrally supported core to produce tubes such as pipes, to very complex sections for curtain tracks or hollow window frames.

### Blow moulding

Blow moulding is a simple process where compressed air is introduced underneath a warmed sheet of thermoplastic material forcing the material into a mould cavity, or allowing it to expand freely into the shape of a hemisphere.

It is a good way of forming large domes, which when made out of clear acrylic sheet are often used in shop displays.

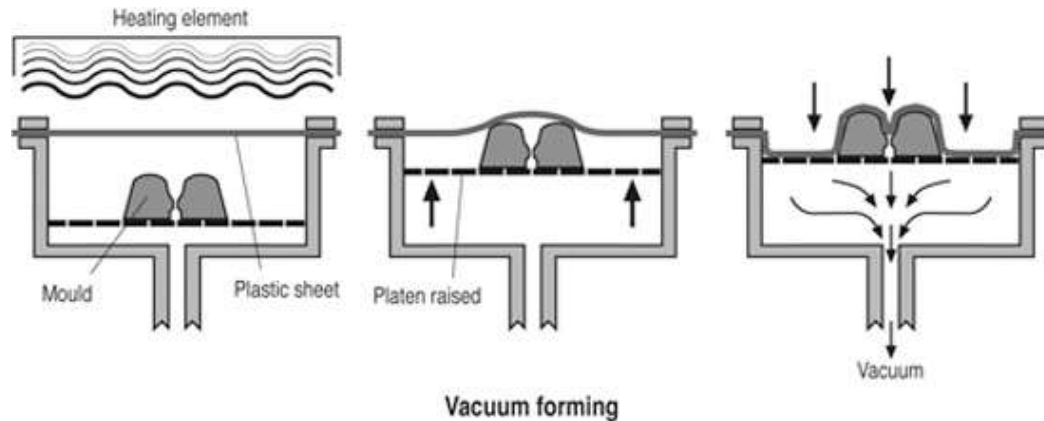


Blow moulding

### Vacuum forming

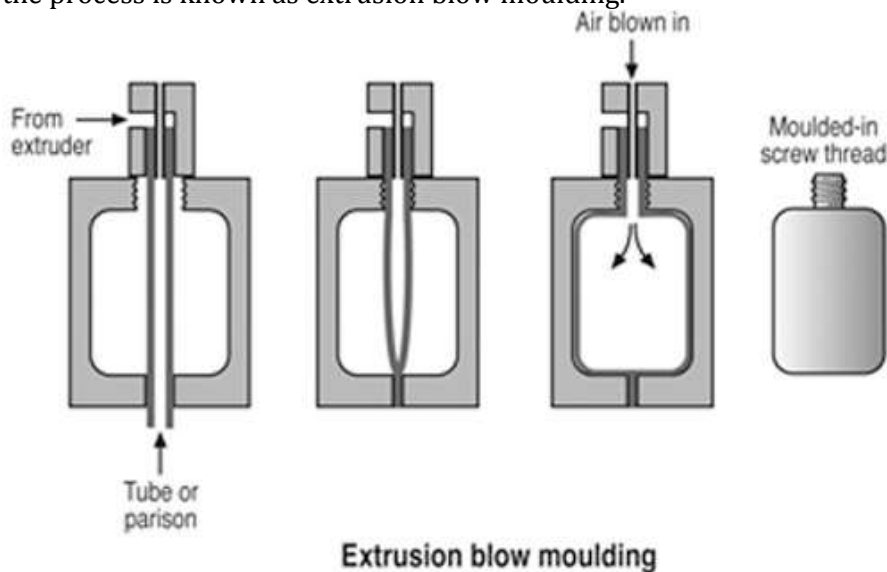
This is a very common manufacturing process used, for example, to make a range of plastics packaging. Think of the boxes sandwiches come in, or the inner in a chocolate box, or your acrylic bath. It is really the opposite of blow moulding. Instead of the warmed plastic sheet being forced into a mould by air pressure, in vacuum forming the air is drawn out from under the softened plastic sheet, so it is forced over or into a mould by atmospheric pressure.

Vacuum forming is a very common and effective way of producing complex shapes in thermoplastic sheeting.



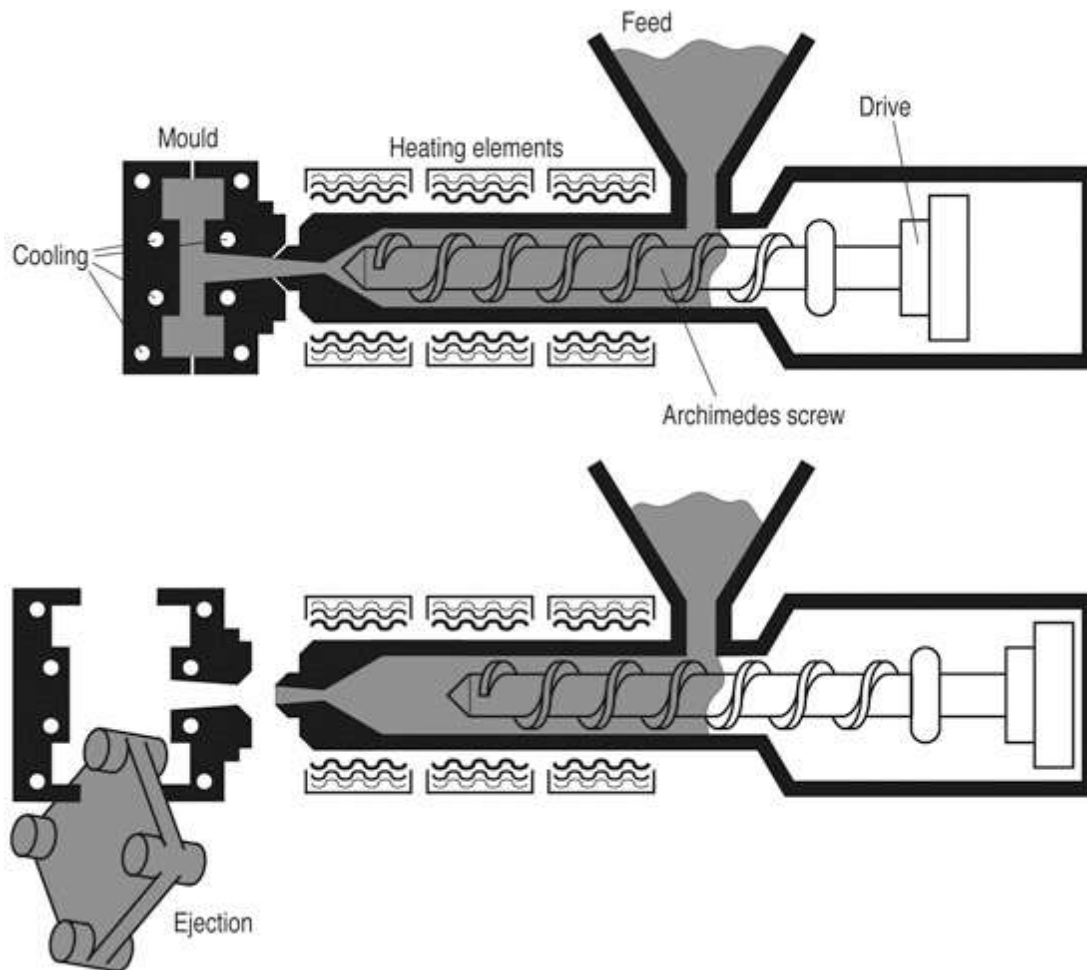
### Extrusion blow moulding

This is a combination of extrusion and blow moulding and is often used where the article to be made has a narrow neck, such as a bottle. The plastic material is first extruded as a tube shape into an open die. The die is then closed to seal the ends of the tube and air is blown in forcing the plastic tube to take up the shape of the die cavity. As the material is extruded first and then blow moulded, the process is known as extrusion blow moulding.



### Injection Moulding

This process is one of the most common of all plastics manufacturing processes. The polymer, in granule form, is heated until fused and forced into a closed mould. Because of the viscous (thick, syrupy) nature of the fused polymer, very high pressures are needed to make it flow, which means that the machine and mould have to be very strong to withstand the forces involved.

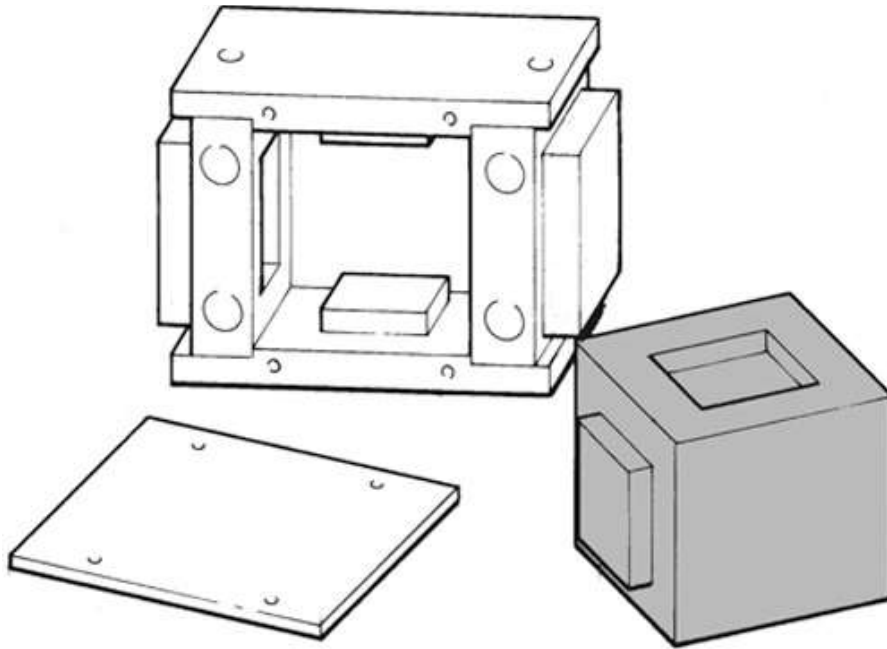


Injection moulding

A typical industrial injection moulding machine uses a screw to force the granules along a heated barrel, and when the granules become fused the screw is used as a plunger to force the polymer into the mould. The moulds are usually made from high-grade steel to withstand the forces involved and must also be highly polished to produce a very good finish on the product, as any scratches will show up in the moulded plastic surface. Because of the ability of the plastic to show even the smallest of marks very fine detail can be cut into the surface of the mould, for example in the form of trade marks, lettering or textures.

### Rotational Moulding

Rotational moulding is used to produce hollow thermoplastic products such as drums, storage tanks and litterbins. A carefully calculated amount of plastic is placed in a closed mould that is heated in an oven and rotated slowly around both a vertical and horizontal axes. The plastic material fuses and sticks to the hot mould surface, building up the required thickness. The mould is then gradually cooled by air or water while still rotating. The mould is opened, the finished product removed and the mould reloaded and closed for the next cycle. The time it takes to make one of the products is known as the product's cycle time.



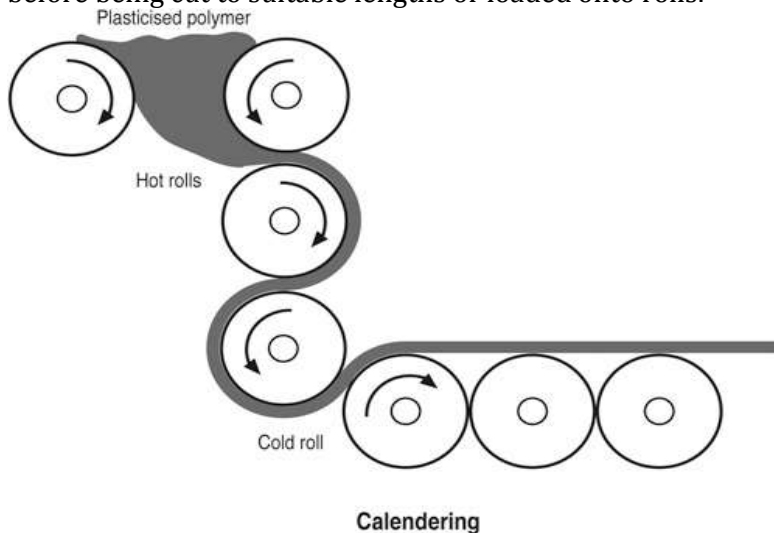
Rotational moulding

### Foaming

Plastic foams used in packaging and the upholstery industry can be produced by using blowing agents that are mixed with the base polymer. When heated these agents release gas which form bubbles in the plastic. Another method is to inject compressed nitrogen gas into molten plastics during the moulding process. A third method is to freeze a gas within the plastics granules which then expands due in the heat of the moulding process.

### Calendering

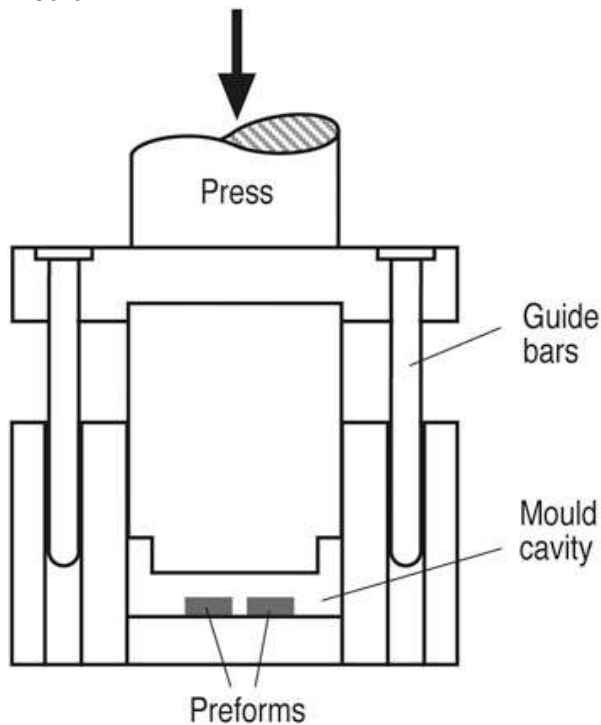
Calendering is used to produce plastic sheeting and products such as floor tiles, coated fabrics and coverings for car interiors. Fused thermoplastic is extruded on to heated rotating rollers that squeeze the material into a continuous sheet or film. The film is cooled by jets of air or water, before being cut to suitable lengths or loaded onto rolls.



### Compression moulding

Compression moulding is one of the oldest manufacturing technologies associated with plastics and was used in 1854, for example, by Samuel Peck to make picture frames from shellac mixed with wood flour. The process is almost always used with thermosetting plastics. A carefully weighed amount of thermosetting polymer is placed into a preheated lower mould cavity. The mould is then closed by the placing of the upper half and subjected to further heat, and pressure provided by a press, often of several hundred tons capacity.

The pressure and heat causes polymerisation and the flow of the plasticized material within the mould.



### Compression moulding

Raw thermoplastic materials containing fillers may be compressed whilst cold into small blocks of predetermined weight called preforms. Using preforms in compression moulds saves having to weigh out powdered material each time the mould is filled and decreases the cycle time, as the preforms may be preheated.

A development of compression moulding is transfer moulding. In this process the thermosetting polymer is first loaded into a heating chamber above the mould cavity and allowed to polymerise. It is then squeezed through channels into the mould cavity by the action of a powerful press. Transfer moulding is used when complex mouldings are required and the polymer needs to flow quickly around the mould cavity.

Many plastic articles have metal parts included within them during the moulding process. These metal parts are called inserts, and may, for example, be in the form of captive nuts used in conjunction with bolts to hold other parts of the final product assembly. The inserts are placed in recesses in the lower mould either by hand or by using loading jigs before the polymer is introduced into the mould. Compression and transfer moulding are manufacturing techniques that lend themselves to the inclusion of moulded inserts. When inserts are used the technique is often termed insert moulding.



**Plastics and the Environment**

There are three possible environmental problems to be considered. Firstly, plastics are mostly made from oil, natural gas or coal, and these are all limited natural resources that must be conserved. Secondly, the manufacture of plastics produces a lot of harmful pollutants which manufacturing companies need to deal with properly. Thirdly, old and unwanted plastics are not always easy to dispose of. Buried in landfill sites they will take a very long time to rot.

To reduce these problems plastics must be 'designed' (for example as biodegradable), manufactured, used and disposed of considerately.

The very properties, which have made plastics such a necessity to modern living, may well present problems once their useful life has finished. Plastics are used as paints, cable coverings and window frames as they do not rot, and they are therefore very difficult to degrade when their useful life is over.

Plastics which are used in motor vehicles are very durable and corrosion resistant which also means they are very resistant to degradation. Plastic food packaging increases the shelf life of foods, and provides a cheap, hygienic and very versatile range of wrappings. Although there are obvious advantages for the food industry, the huge increase in plastic packaging has greatly increased plastic waste, and consequently, litter.

In the manufacturing process a certain amount of waste plastics are produced as sprues and runners, (the inlets into injection moulds) and other forms of excess material. To reduce waste, this material can be reground and added back to new raw stock. Though this is possible with most thermoplastic materials, the same is not true for thermosetting materials as the addition of even quite small quantities of re-ground material can reduce the quality of the final mouldings.

Although plastic litter is very visible, the problem of plastics waste has to be seen in perspective. Plastic waste which does not degrade means it will not produce dangerous gases such as methane which can make landfill sites hazardous. This of course is no justification for simply dumping plastics waste and to ensure plastics are correctly disposed of alternative methods must be used.

Most plastics are made from petroleum and could be used as a fuel alternative, since many have an energy value similar to coal. Recycling by burning to produce energy would save raw materials such as crude oil and coal, and the gases produced through burning plastics are also valuable resources, which may be recycled.

An alternative way of recycling plastics is collection and reprocessing.

Although recycled materials might be inferior in quality, there is still a wide range of products where the quality is not an essential factor, such as dustbin bags. The main problem with recycling plastics is their collection and sorting.

Some very expensive machinery is needed to separate and wash the material, which is then granulated and reused in a similar range of applications to the original. Food packaging is an exception.

Plastics are increasingly used in the motor vehicle industry as they are light in weight, self coloured, impact resistant and readily shaped to make single integrated rather than fabricated components. The motor industries are therefore being pressured into providing recycling facilities for vehicles that have reached the end of their lives. The number of different plastics used is being reduced and those used are nowadays marked for identification. With the backing of the multinational motor

companies, plastics recycling is being driven forward and new technologies are being developed which will eventually be used for domestic plastics waste.

### **Common Plastics - their abbreviations, names and uses**

#### ***Thermoplastics***

##### *Acrylonitrile butadiene styrene ABS*

Computer housings, car bumpers, camera bodies, telephones, suitcases.

##### *Cellulose acetate CA*

Spectacle frames, toothbrush handles, packaging film.

##### *Polymethylmethacrylate PMMA Acrylic*

Jewellery, display stands, shop signs, lenses, synthetic fibres.

##### *Polyamides Nylon*

Clothing, gears, bearings, zips.

##### *Polycarbonate*

Bullet proof shields, bottles, crash helmets.

##### *Polyethylene Polythene*

Carrier bags, kitchen containers, children's toys.

##### *Polypropylene*

Furniture, ropes, electric kettles, door handles, hinges.

##### *General purpose polystyrene GPPS*

Packaging, jewellery.

##### *High impact polystyrene HIPS*

Refrigerator inners, radio casings, yoghurt pots.

##### *Expanded Polystyrene*

Insulation, packaging.

#### ***Thermosetting plastics***

##### *Casein*

Buttons.

##### *Epoxy resins Araldite*

Adhesives, coatings.

##### *Melamine formaldehyde Formica*

Decorative laminates.

##### *Phenolic resin Bakelite*

Electrical insulators, ashtrays, saucepan handles, toilet seats.

*Polyester resin GRP*

Glass reinforced plastics used in boatbuilding and car bodies.

*Advanced polyester resin*

Glue gun bodies, power tool casings.

*Polyurethane*

Car bumpers, shoe heels.