Polymer chemistry is a very complex subject. The basic information presented here is sufficient for the reader to gain a good understanding of polymers which forms the base for plastics under which polyurethanes (PUR) are classified.

In ancient times, people used copper, gold, iron and clay for their daily needs, which were found in their natural form in the earth. However, as time passed and technology advanced, people needed to make goods that were strong, malleable, durable, practical and cheap. Materials with these properties could not be found with what was available, so they looked for newer materials, which led to synthetic materials. One such group of materials is plastics.

The word ‘plastics’ is derived from the Greek word plastikos. In general, a plastic material can be defined as a material that is pliable and capable of being shaped by temperature and pressure. Plastics are based on polymers, derived from the Greek word polymeros with poly meaning many and meros meaning basic units. Polymers are also called ‘resins’, which is not really correct because resins are gum-like substances.

3.1 What is a Polymer?

A polymer is a large molecule (‘macromolecule’) composed of repeating basic structural units. These subunits are typically connected by covalent chemical bonds. Although the term ‘polymer’ is sometimes taken to refer to plastics, it encompasses a larger class of compounds comprising natural and synthetic materials with a wide variety of properties. Because of the extraordinary range of properties of polymeric materials, they have essential and vital roles in everyday life. This role, ranges from the familiar synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins, which are essential for life.

Natural polymeric materials such as shellac, amber and natural rubber have been used for centuries. Many other natural polymers exist such as the well-known cellulose, the main constituent of wood and paper. Examples of synthetic polymers (Figure 3.1) are synthetic rubber, neoprene, nylon, polyvinyl chloride (PVC), polystyrene, polyethylene,
Polypropylene, silicone and PUR. The most common continuously linked backbone of a polymer used for the preparation of plastic compounds consists mainly of carbon atoms. A simple example is polyethylene (commonly known as ‘polythene’), whose repeating unit is based on the ethylene monomer, a petroleum byproduct. However, other elements such as oxygen are also commonly present in polymer backbones. Most elements are combinations of two or more atoms bonded together to form molecules.

In plastics, bonding patterns are very important because they determine the physical characteristics of the plastic product. Bonds can be divided into primary bonds (ionic or covalent bonds) and secondary bonds (van der Waals forces). All bonds between atoms and elements are electrical in nature. Most elements constantly try to reach a stable state by (a) receiving extra electrons, (b) releasing electrons, or (c) sharing electrons.

A polymer is made up of many basic units (‘mers’) repeated in a pattern and, if a large number of molecules bond together, a polymer is formed. These basic units are considered to be bifunctional with two reactive bonding sites. Monomers (Figure 3.2) are the initial basic units used in forming polymers and in most cases are liquids. The chemical reaction or process that joins these monomers together is called ‘polymerisation’. If the polymer consists of similar repeating units, it is called a ‘homopolymer’ (meaning ‘the same’). If two different types of monomers are polymerised, it is called a ‘copolymer’. If three types of monomers are polymerised to form a polymer, it is called a ‘terpolymer’ (Figure 3.3) (these are also known as copolymers). An ‘elastomer’ is described any polymer that can be stretched to ≥200% of its original length:

e.g., \[ M + M + M \ldots = \text{homopolymer} \]

\[ M1 + M2 \ldots = \text{copolymer} \]

\[ M1 + M2 + M3 \ldots = \text{terpolymer} \]

In general, polymers are classified by systems based on: source, light penetration, heat reaction, polymerisation and crystal structure:

- **Source**: polymers from natural sources as well as modified natural or synthetic sources.
- **Light penetration**: optical properties (e.g., opaque, transparent or luminescent).
- **Heat reactions**: thermoplastic (soft on heating, solid on cooling; can be re-used).
- **Polymerisation**: methods of joining many monomers (basic units) to form polymers and copolymers.
• Crystal structure: crystalline (molecules arranged in order) and amorphous (random arrangement of molecules).

![Basic polymer structures](image)

**Figure 3.1 Basic polymer structures**

![Basic monomers example](image)

**Figure 3.2 Basic monomers example**
3.1.1 Polymer Synthesis

Polymerisation is based on combining many small molecules known as monomers (basic units) into covalently bonded chains or networks. During this process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerisation of polyethylene terephthalate polyester. The monomers are terephthalic acid and ethylene glycol but the repeating unit is \(-\text{OC} - \text{C}_6\text{H}_4\text{-COO-CH}_2\text{-CH}_2\text{-O-}\), which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct portion of each monomer that is incorporated into the polymer is known as a ‘repeat unit’ or ‘monomer residue’. Laboratory synthetic methods are generally divided into two categories: step-growth polymerisation and chain-growth polymerisation. The essential difference between the two is that in chain-growth polymerisation, monomers are added to the chain one at a time only whereas, in step-growth polymerisation, chains of monomers may combine with one another directly. Synthetic polymerisation reactions may be carried out with or without catalysts.

3.1.2 Modification of Natural Polymers

Many commercially important polymers are synthesised by the chemical modification
of naturally occurring polymers. Prominent examples include the reaction of nitric acid and cellulose to form nitrocellulose as well as the formation of vulcanised rubber by heating natural rubber in the presence of sulfur. Some of the ways in which polymers can be modified include oxidation, crosslinking and end-capping.

3.2 Polymer Properties

Polymer properties can be divided into several classes based on the scale at which the property is defined, as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as ‘microstructure’, describes the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major part in determining the bulk physical properties of the polymer (which describe how the polymer behaves as a continuous macroscopic material). Chemical properties describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

3.2.1 Monomers

A monomer (basic unit) of a plastic material is the initial molecule used in forming a polymer. If a large number of molecules bond together, a polymer is formed. One of the most important and common monomers is ethylene gas resulting from the refinement of crude oil, which is liquefied. Most monomers are liquids.

Monomers form five basic structures: (i) linear, (ii) crosslinked, (iii) branched, (iv) graft, and (v) interpenetrating. If two different monomers are joined in sequence, it is called a ’co-polymerisation’ and a copolymer plastic material is the result:

1. Linear structures – There are three basic linear copolymer classes:
   - Alternating – ABABABAB...
   - Random – ABBAABAAABAB...
   - Block – AAAABBBBBBAAA...

2. Crosslinked structures – involve primary covalent bonds between the molecular chains. AAAAAAAAAAAAAAAAAAAAAAAA
   /                     /
   B                        B
   B                        B
3. Branched structures represent three-dimensional branching of the linear chain.

4. Graft structures – graft polymers are similar to crosslinked and branch-structured copolymers. The term ‘graft’ has been used to denote a controlled or engineered addition to the main polymer chain.

5. Interpenetrating structures – these polymer networks are an entangled combination of two crosslinked polymers that are not bonded to each other. A ‘plastic alloy’ is formed if two or more different polymers are physically mixed together in the melt. The term ‘polyblend’ refers to a plastic that has been modified by the addition of an elastomer.

The identity of the monomer residues (repeating units) forming a polymer is its first and most important attribute. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. Polymers that contain only a single type of repeating unit are known as homopolymers, whereas polymers containing a mixture of repeating units are known as copolymers. Polystyrene, for example, is composed of only styrene monomer residues and is therefore classified as a homopolymer. Ethylene vinyl acetate contains more than one variety of monomer and is thus a copolymer.

3.2.2 Microstructure

The microstructure of a polymer (sometimes called ‘configuration’) relates to the physical arrangement of monomers along the backbone of the chain. These are the elements of polymer structure that require breaking of a covalent bond in order to change. Structure has a strong influence on the other properties of a polymer. For example, two samples of natural rubber may exhibit different durabilities even though their molecules comprise the same monomers.

An important microstructural feature of a polymer is its architecture, which relates to the way branch points lead to a deviation from a simple linear chain. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Types of branched polymers include star polymers, comb polymers, brush polymers, dendronised polymers and dendrimers. The architecture of a polymer
affects many of its physical properties, including (but not limited to) solution viscosity, melt viscosity, solubility in various solvents, glass transition temperature \((T_g)\) and the size of individual polymer coils in solution. Various methods may be employed for the synthesis of a polymeric material with a range of architectures.

### 3.2.3 Chain Length

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase. Impact resistance also tends to increase with chain length, as does the viscosity or the resistance to flow of the polymer in its melt state.

A common means of expressing the length of a chain is the degree of polymerisation, which quantifies the number of monomers incorporated into the chain. As with other molecules, the size of the polymer may also be expressed in terms of molecular weight. Synthetic polymerisation methods typically yield a polymer product including a range of molecular weights, so weight is often expressed statistically to describe the distribution of chain lengths present. Common examples are the number average molecular weight and weight average molecular weight. The ratio of these two values is the polydispersity index. A final measurement is contour length, which can be understood as the length of the chain backbone in its fully extended state.

### 3.2.4 Molecular Mass (Weight)

The mass of a molecule is determined by adding together the atomic masses of the various atoms making up the molecule:

e.g., the atomic mass of hydrogen is 1 and that of oxygen is 16.

Thus, the molecular mass of a single molecule of water \((H_2O)\) = 1 + 1 + 16 = 18.

The length (molecular mass) of a polymer chain has a profound effect on the processing and properties of a plastic compound. Increasing chain length may increase toughness, melt temperature, melt viscosity, creep and stress resistance. It may also increase the difficulty of processing, material costs and possible polymer degradation.

### 3.2.5 Polymerisation

The mechanism or chemical reactions that join the basic monomers is called
polymerisation. Polymerisation falls into two general categories: addition and condensation.

Most polymers are produced by addition polymerisation. In this process, unsaturated hydrocarbons are caused to form large molecules. The mechanism of the reaction involves three basic phases:

- Initiation – the phase in which the monomers are caused to join by the aid of a high-energy source, such as a catalyst or heat source.
- Propagation – the addition process continues.
- Termination – the final product: a polymer has been produced and the process is caused to stop.

**3.2.6 Condensation Polymerisation**

Condensation is a chemical reaction in which a small molecule (often water) is eliminated from the polymer.

Plastic compounds are formed by the addition of additives such as fillers, solvents, stabilisers, plasticisers and colourants to these basic polymers. These additives influence many characteristics of the final products. Plastics are categorised into two main groups: thermoforming and thermosetting. In the former, a plastic material softens on heating and can be reused, whereas thermosetting materials harden on heating and cannot be reused. It is the molecular arrangement of a polymer that determines the category. Examples of thermoforming plastic resins are polystyrene and polyethylene, whereas examples of thermosetting are polyurethanes and silicones.

**3.3 Mechanical Properties**

The mechanical or bulk properties of a polymer are of primary interest for processing because they dictate how the polymer behaves in use.

**3.3.1 Tensile Strength**

The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation. This property is very important in applications that rely upon the physical strength or durability of a polymer. For example, a rubber band with a higher tensile strength will hold a greater weight before