PLASTICS AND POLYMERS
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12·1 Introduction

Synthetic organic polymers are the most widely used new materials of the 20th century. Their ancestors, naturally occurring macromolecular materials such as natural rubber, wood, cotton, wool and hardened oils, have been known for much longer and valued for the qualities conferred by their basic structure, but the first synthetic polymers were not produced until the 19th century. Synthetic polymers now dominate so many applications—not only as plastics and rubbers but also as fibres, paints and adhesives—that the rate of increase in their consumption is an important barometer of an industrial economy. In this chapter we concentrate mainly on the use of polymers, usually compounded with various additives (e.g., pigments and fillers), to form solid plastics from which components and structures can be formed.

Most early plastics were thermosets, such as phenol formaldehyde (filled with wood flour to produce 'Bakelite') and melamine formaldehyde. These cure (set) permanently during forming into their final shape, and are subsequently quite heat-resistant. A second major class of polymers, the rubbers or elastomers, also owe their spectacular elastic properties to a post-moulding process during which they set and acquire stability. The majority of polymers consumed nowadays are thermoplastics, principally the ‘commodity’ thermoplastics polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP) and polystyrene (PS). These are repeatedly remouldable under heat and pressure, making their conversion into finished products particularly rapid and economical. The price for this re-formability is their relative sensitivity to temperature, and in particular their tendency to creep under load. Outside the electrical industry, in which their intrinsic high resistivity and dielectric properties were exploited relatively early, these materials originally gained popularity less on their excellence in performance than on their convenience as substitutes for other materials, offering low cost per unit volume, easy processability, and good decorative qualities or transparency.

Since the mid-1970s, however, this situation has changed rapidly. While the cost of the commodity thermoplastics has increased considerably (helping to outdate ‘cheap plastic’ as a term of abuse), greater understanding of the relationships between their molecular structure and their bulk properties has directed the steady introduction of new grades, spectacularly improved by modification, blending or filling. The well-established use of a polyamide (PA, ‘nylon’) in engineering components had already spearheaded a new
A wave of high-performance 'engineering plastics' such as polycarbonate (PC) and polyoxymethylene (POM, 'acetal'), which have gained respect as reliable load-bearing materials. More recently, it has virtually become possible to design a special polymer to a particular portfolio of required properties. Some of these new polymers offer mechanical performance or physical properties which would have seemed unattainable in 1970.

Underlying the enormous diversity of plastics and polymers are common structural features, which distinguish them as a class of material very different from those which we have considered so far. It is the relationships between these structural features and properties which this chapter will introduce. Since the final properties of these materials are heavily influenced by their history and the method by which they have been formed, we will also consider the techniques used to do so.

12.2 Molecular structure

12.2.1 Monomers and polymers

Polymers are defined by their molecular structure: they contain long, covalently bonded chains of repeated sub-units (mers). These chains are sometimes branched, and sometimes interconnected at points along their length (by branch chains or by short crosslinks) to form a network.

A homopolymer is constructed from a single type of mer. The distinctive characteristics of a polymer can be illustrated by comparing linear polyethylene, whose molecule is a very long chain of \(i\) ethylene mers \([-\text{C}_2\text{H}_4\text{-}]_i\), with the linear alkane series, \([-\text{C}_2\text{H}_{4i+2}\text{-}]\) (Fig. 12.1). Starting from ethane \((i = 1)\), the alkanes show steadily changing physical properties as \(i\) increases.

![Diagram of ethylene monomer and polymer chains](Fig. 12.1) Structure of polyethylene. Opening of the double bond in ethylene gas (a) forms an active ethylene mer (b) which can form chains. Chains with hydrogen end-caps are alkanes (c). Above a critical chain length neither the end-groups nor the chain length affect properties very much; these are polyethylenes.