Materials Science in Design and Engineering

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Preface

Human activities will always rely on the availability of materials. It can be expected that in view of the increasing complexity of products the range of materials will become larger and larger. This not only applies to the modern materials, but also to the classical materials still in use since the very start of human activities: ceramics and biomaterials. Moreover, modern products are assemblies of different materials. Materials science and materials selection therefore become more and more important and are integrated parts of product development. This process often starts with design sketches on the basis of a more or less explicit list of requirements and iteratively runs *via* materials selection, selection of the manufacturing process, manufacturing and market introduction until scrap processing. In a sustainable world this chain should be a cradle-to-cradle concept. In each part of the chain, materials and materials science play their role. So, for designers and engineers it is of great importance to have knowledge of materials.

This book is an introduction to the very broad range of materials that is relevant for modern designers and engineers when designing and manufacturing new products or improving existing ones. The book provides designers and engineers with basic knowledge and insight in order to better cope with problems and questions arising when designing and manufacturing specific products. One may wonder if in an era dominated by an abundance of free internet information, textbooks like this one still play a role. In our opinion the answer is affirmative. The designers' or engineers' knowledge and insights are essential in the search for suitable materials, as they form the framework in which new information can be judged.

In many cases, materials selection starts with the translation of product requirements into material properties. Hence, properties play a key role in materials selection. As a matter of fact, a designer is often more interested in certain material properties than in the material as such, since the material is only bearer of the required product properties. Then the following questions arise: what is a property and which properties are important? These questions are dealt with in Chapter 2. In the subsequent chapters the structure of materials and the material classes are discussed. The book ends with chapters devoted to the manufacturing processes and materials selection. The latter issue is highlighted from different points of view and illustrated with a practical example.

For the present (and first English) edition a new co-author, prof. dr. S.J. Picken, has strenghtened the team. This new cooperation has led to innovations related to his personal expertise: functional polymers. Prof. em. dr. B.M. Korevaar made a useful contribution to the present text by reviewing

Chapters 2 to 5. Materials of biological origin have served mankind from the earliest days of human activities. They still play an important role in modern life (textiles, leather and wood). In principle, biological materials offer the possibility of an endless supply and as such they are fully compatible with the demands of sustainability. Therefore it was decided to devote a new Chapter (8) to this class of materials. The inspiring discussions with dr. J. van Dam (Wageningen University) are gratefully acknowledged, whereas the scientific director of the Botanical Garden of Delft University of Technology, drs. W.N.J. Ursem, critically reviewed this chapter. The Section about concrete in Chapter 9 was rewritten in close collaboration with dr. M. de Rooij and dr. A. Fraaij (both from the Faculty of Civil Engineering and Geosciences of Delft University of Technology). Chapter 10 about processing and manufacturing was completely rewritten after fruitful discussions with ir. C.A. van Luttervelt (retired from the Faculty of Mechanical, Maritime and Materials Engineering of Delft University of Technology) and dr. A. Hoogstrate (TNO, Eindhoven, The Netherlands). Finally, the Appendix on Standardization and nomenclature was updated in collaboration with drs. H. van der Hoek (Dutch Normalization ,nstitute NEN) and dr. H. de Vries (Erasmus University of Rotterdam, The Netherlands).

We hope that designers and engineers will benefit from the new features of this book. We are indebted to the publisher, mr. J. Schievink, for his involvement and enthusiasm.

Delft, Spring 2012 Pieter van Mourik, Jaap van Dam, Stephen Picken

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Chapter 1

Introduction

Matter transforms into a material when it is applied in a lasting solid product. Hence, materials selection is an integral part of the whole designing process. For all materials, there is a strong relation between the composition, the method of production and the final resulting properties of the product. This will be discussed, in different contexts and on different occasions, throughout the course of this textbook. This discussion does not start from scratch as everybody has, at least some, knowledge of common materials. In the field of industrial design and engineering, the following classes of materials are important:

1. Metals
2. Biomaterials
3. Synthetic polymers
4. Ceramics

Metals and metal alloys can be lustrous, are often ductile and when touched, feel cold. Everybody knows iron and steel. The applications of iron and steel are so dominant that metals are divided into ferrous and non-ferrous metals. On a mass basis, the annual worldwide production of iron and steel is fifty times larger than that of the second-ranked metal: aluminium and its alloys. This dominant position is especially related to the low cost of mining and refining, and the enormous variation in properties of iron and steel alloys.

Biomaterials are all materials from natural origin, like wood, leather, wool, and the fibres of vegetable origin (hemp, flax, cotton and jute). Natural rubber occupies a position in-between: its origin is biological, but as far as structure and processing are concerned it resembles a synthetic polymer.

Synthetic polymers are generally derived from mineral oil. They are of paramount importance for the designer: from use in simple domestic appliances and low-cost packaging materials to advanced fibres that are stronger than steel, and for insulating materials and protective coatings that can withstand years of exposure to harsh conditions.

Ceramics form the oldest class of materials used in human civilization. Ceramic pots were already in use 15,000 years ago and glass dates back to about 50 centuries BC. For the designer and the engineer these materials are important because of their wide range of properties: good conductors or good insulators for heat and electric currents, high heat resistance, often in combination with sustainability in a wide variety of environments. Often, the ceramic material is formed during the manufacturing process of a certain product. Here again, the link between composition, the manufacturing process and the resulting properties of the product is crucial.

Generally, the designer is asked to design a whole product, which is mostly an assembly of different parts, each in turn consisting of a variety of materials. The whole product has to meet the demands specified by the list of requirements. Performing a rational materials selection in relation to the total design will thus be complicated. In a successful industrial design, all the aspects: engineering, materials selection, cost and sustainable manufacturing, are balanced. To obtain this balance, the importance of industrial design for mass production has to be acknowledged in an early stage of product development. For example, a long time ago the Dutch United Glassworks at Leerdam started producing a series of glasses designed by Copier, which combines artistic functionality with the demands of mass production. This resulted in a well-known *interbellum* design, the so-called tulip glass, which is still in production at the beginning of the 21st century. However, here the materials selection is traditional: as wine is to be drunk from a glass, this product is entirely made of glass — not out of polymers or metals. Alternatively, the use of polymers for packaging of beverages has become widespread in recent years and this is based on a rational rather than a traditional choice.

For a rational materials selection, and hence for a good design, knowledge of materials and their properties is essential, Also, from a practical point of view, an overall insight in costing (cost effectiveness), availability, processing and environmental impact of materials use is necessary. In view of the above, the Faculty of Industrial Design of Delft University of Technology listed the following requirements for Materials Science Education (Marinissen *et al.* (1992)):

1. Knowledge of materials, especially metals and polymers; their physical and chemical properties in relation to function, their manufacturing, and the environmental impact of goods obtained by mass or series production.
2. Knowledge of the availability of materials: forms, types and quantities.
3. Ability to understand and evaluate materials data from handbooks.
4. Understanding the relevance of materials for industrial design and for mass and series production.
5. Knowledge and understanding of the application of metals and polymers in relation to requirements on function, manufacturing and cost effectiveness.
6. Knowledge and understanding of the process of materials selection.
7. Insight in the trends and modern developments in materials science.

The common feature of these requirements is that the student gains insight into the relation between materials selection, product design and product manufacturing. This is the basis for a rational selection of materials and it will be highlighted throughout this textbook for metals, polymers, ceramics and some examples of biomaterials.

As stated before, in many products a large variety of materials is used. During the design the question "Which application and which material is most suited for this product?" will regularly arise. The complexity of this question will be illustrated by the following example.

A coffee machine is much more complicated than appears at first sight. Every part has its specific function. Think of the heater, the heat exchanger, the water pump and the casing in which all parts are assembled. For each part, functional and manufacturing requirements have to be considered and a proper materials selection has to be performed. For every stage of the design process the question is "Does the selected material meet the set functional and manufacturing requirements?". Table 1.1 lists a few of the requirements for the casing of a coffee machine.

Table 1.1. Functional and manufacturing requirements for the casing of a coffee machine.

functional	*manufacturing*
cold water storage	one-piece manufacturing
transport of hot water (about 80°C)	no finishing
protection of the coffee pot	low cost
lasting durable colour	suitable for mass production
light weight, *i.e.* low mass	

The designer starts the design process by gathering the functional and manufacturing requirements. Establishing the requirements to be met is absolutely essential, as these requirements allow suitable and unsuitable combinations of properties to be specified.

Table 1.2. Required material properties.

functional	*manufacturing*
hot and cold water resistant	suited for injection moulding
scratch resistant and good impact strength	low materials costs
durable colour without finishing	
no adhesion of coffee stains	
resistant to common detergents	

Each material represents a combination of desired and less desired properties. However, a designer has no interest in a material as such. Instead his interest involves choosing the material with (at least) the properties that meet the functional and manufacturing requirements (see Table 1.2).

Many polymers can be processed easily *via* injection moulding (see Chapter 10), during which a complicated item can be formed without or nearly without additional processing steps. For example, pigments can be blended with the polymer resulting in a coloured product without the need of finishing treatments like painting. Polymers are available in an enormous variety. An important subdivision is into rubbers, thermosets and thermoplastics. As a coffee machine made out of rubber does not seem very practical, thermosets and thermoplastics are the remaining possibilities. As will follow from Chapter 10, only thermoplastics are easy to process *via* injection moulding with a minimum of final processing. The material selection is now restricted to finding a thermoplastic that best meets the requirements. The primary selection will be performed on the basis of a quantitative comparison between the requirements and the available thermoplastic polymers. Practical considerations, *e.g.* cost and availability of machinery for the planned numbers of production, are often decisive for the final selection.

Problem 1.1 *Estimate the number of coffee machines annually sold in a West European country of about 16 million inhabitants.*

In modern society the list of available materials is so large that not all materials can be covered by a textbook. However, it is important for the designer to have an overview, as this offers a framework for selection. As matter transforms into materials by virtue of their application, obtaining this overview is greatly enhanced by thinking of specific products and the materials that are commonly used to make them. One can group materials into a limited number of classes. These and some products made of them are shown in Table 1.3.

Table 1.3. Classification of materials.

product	*common name of applied material*	*classification*
tea cup	porcelain	ceramics
oven dish	Pyrex	glass
beverage can	tin	ferrous metal
aeroplane	aluminium	non-ferrous metal
bicycle tyre	rubber	polymer
book	paper	biomaterial

Table 1.4 presents an overview of materials, divided into metals, synthetic polymers, biomaterials and ceramics. The division between heavy and light metals lies at a density of 4500 kg/m^3. For an overview of materials it is convenient to describe the various features of the different materials. These features can be used to distinguish between them; for example, a simple magnet can be used to discriminate between magnetic and non-magnetic

materials. Besides these features, some typical applications will be given in the following sections. Of course, these descriptions of features and applications will be broad: general characteristics prevail above details.

Table 1.4. Overview of materials.

class	*category*	*examples*
ferrous metals		carbon steel
		alloy steel
		cast iron
		cast steel
non-ferrous metals	light metals	aluminium + alloys
		magnesium + alloys
		titanium + alloys
	heavy metals	copper + alloys
		zinc + alloys
		nickel + alloys
		tungsten + alloys
synthetic polymers	thermoplastics	polyethylene
		polypropylene
		polyvinyl chloride
		polyester
		polyamide
	thermosets	Bakelite®
		epoxy resin
		polyester resin
	rubbers	styrene-butadiene rubber
		silicone rubber
	composites	glass fibre-reinforced polyester
		carbon fibre/epoxy composites
	foams	polystyrene foam
		polyurethane foam
biomaterials	wood	cellulose
		paper pulp
	rubbers	natural rubber
	thermoplastics	starch
		polyactic acid, polyhydroxyalkanoate
		cellulose diacetals
	thermosets	furan resin
		lignin
		alkyd resins
	(textile) fibres	cotton, flax, hemp, jute
		wool, silk
	composites	linoleum
		fibre board

class	*category*	*examples*
ceramics	minerals	silica (quartz) gem stones
	classical ceramics	earthenware bricks concrete
	technical ceramics	alumina, zirconia titanium nitride silicon carbide diamond

1.1 Metals

Metals can be polished resulting in a lustrous surface, but exposed to air many metals cover themselves with oxide layers yielding a matt appearance. Only the precious metals keep their lustre. Most technical metals are incombustible with a few notable exceptions such as magnesium. They melt at high temperatures and show excellent electrical and heat conduction. Metals are heavy compared to polymers and feel cold due to their high thermal conductivity. Metals show impressive strength, often in combination with tough and/or ductile behaviour.

1.1.1 Ferrous metals

Iron and steel

Iron and steel rust when exposed to water and air, until finally a hole develops. Iron and steel are heavy, strong, and are (usually) magnetic. Steel is available as tubes, U, I, H and L profiles, and as plates: very thick for ships, thinner for refrigerators and cars, and very thin for packaging (cigar boxes and beverage cans). Steel plates and profiles can easily be welded. Steel is cheap and strong. A great variety of tools, like hammers and pliers, both for home and industrial use, are made of steel. The rods used in reinforced concrete are made of specially heat treated steel. Stainless steel is made stainless by alloying it with about 13 wt% chromium. After alloying it remains magnetic. Non-magnetic stainless steel contains in addition about 18 wt% nickel.

Cast iron

In practice, cast iron is surprisingly sustainable despite the problem of rust. The former pier at the Dutch Scheveningen seaside resort was constructed in cast iron. The lids covering drains in the streets are mostly made of cast iron. Cast iron can be cast in a large variety of complicated forms. The old-fashioned lamp-posts on the Delft Market Place, ‘*les bouches de métro*’ in

Paris and the statue of Rembrandt in Amsterdam are all made of cast iron. Cast iron can hardly be loaded by tensile stresses, but it is able to withstand high compressive stresses. The cast iron columns of the railway station 'Den Haag Hollands Spoor' in The Hague demonstrate this remarkable property by still easily bearing the roof over the platforms since 1888.

Cast steel

The melting temperature of steel is much higher than that of cast iron. Hence, casting steel is much more difficult than casting iron. Complicated high performance parts and expensive machinery are often manufactured of cast steel.

1.1.2 Non-ferrous metals

Aluminium and magnesium alloys

Aluminium alloys are light, do not rust through, but do deteriorate in acid and alkaline environments. They are not as light as plastics, but much lighter than steel. Aluminium alloys are not magnetic. Inevitably, they have a silver-white aluminium colour, but the alloys with silicon are much greyer than the other aluminium alloys. Most aluminium alloys are not as strong as steel. The stiffness of a product made of an aluminium alloy is much lower than that of the corresponding steel product of the same dimensions. In general, aluminium alloys are not as cheap as steel alloys. Pure aluminium is even easier to deform than pure iron. The melting temperature of aluminium is much lower than that of iron or steel. Magnesium alloys are lighter than aluminium alloys. They readily oxidize, and the oxidation process under normal circumstances continues steadily, albeit very slowly. At ambient temperatures, magnesium alloys are very difficult to deform plastically. Hence, processing of magnesium mainly takes place by casting and injection moulding. Machining is very fast and easy although there is a problem: machining yields highly combustible waste in the form of magnesium powder and turnings.

Titanium alloys

The density of titanium alloys is lower than that of iron and steel, but higher than that of aluminium and magnesium. Titanium parts do not rust and the surface remains lustrous when polished, showing an outstanding resistance to harsh environments. The strength of titanium alloys can equal that of steel, but the modulus is lower which means that the resulting stiffness of titanium parts is lower than that of steel parts of the same dimensions. Nevertheless, the ratio of strength to density is very favourable compared to steel. Unfortunately the limited deformability of titanium alloys is an additional problem in the shaping of products, which together with the high price of titanium means that its use is limited to advanced applications.

Copper and zinc alloys

Unalloyed copper is extremely suitable for conduction of heat and electricity. Also, the possibilities for deformation at ambient temperatures are remarkable. On the other hand, copper alloys can obtain strengths as high as steel. Polished copper shines nearly like gold. However, air-exposed copper surfaces often become greenish by forming copper salts. Alloys of copper and zinc are called brass and have a yellow colour. Alloys of copper and tin are called bronze. Coins of low value are often made of bronze. Copper alloys possess a good resistance to (sea) water corrosion. Copper alloys are never magnetic. Zinc alloys melt at very low temperatures. When melted, they possess a very low viscosity, comparable to water. Therefore they are easy to cast and this (used to) result in applications like Dinky Toys and model trains. Zinc alloys are resistant to rainwater. As ambient temperatures are rather high compared to the melting temperature of zinc alloys, the deformation of zinc sheets is rather easy, resulting in applications in gutters and rain pipes. Coating steel products with zinc is called galvanization. Old-fashioned galvanized dustbins and the galvanized steel portals carrying the overhead wires of electric railways have a long life and hardly require maintenance.

Nickel and tungsten alloys

Nickel alloys can be deformed rather easily at ambient temperatures. They are quite precious and hence chemically inert. For this reason nickel alloys are used in coins. Tungsten alloys have a very high melting temperature. For example the filaments in electric light bulbs are made of tungsten.

Gold and silver alloys

Gold alloys show an excellent resistance to a wide range of harsh chemical environments. Silver also, but it unfortunately becomes tarnished when exposed to air. Gold and silver alloys show very good conduction of heat and electricity. Hence, electrical contacts in a large number of electronic devices are plated with silver or gold. Their use in jewellery is a very specific application. Here the ease of deformation is important. The colour of gold alloys strongly depends on the alloying elements used: more towards red when using copper, and more towards white with nickel or palladium.

1.2 Polymers

Many of the useful plastics, rubbers and fibres are synthetic polymers. Most of them are organic in origin. The raw materials are furnished by the coal industry and, chiefly, the petrochemical industry. Synthetic polymers are rather new materials. After a modest start just before and during World War II, their use has increased exponentially. Being new, unknown materials, plastics were in some cases used incorrectly and as a result they became surrounded with an aura of disrepute for many years. In due course it was appreciated, however, that it is unfair to blame the plastics themselves. The significant contribution of plastics to the standard of living is now fully recognized and nowadays production on a volume basis has outstripped that of metals. Polymers are light in weight, some even float on water. In any case, they are always much lighter than metals. Polymers consist of very large molecules, forming very long chains primarily consisting of carbon atoms. Polymers are often transparent. They can be coloured by the addition of pigments. Using soluble pigments, coloured polymers can retain their transparency. However, most pigments, are insoluble in the polymer, so most coloured plastics are opaque. Apart from colourants, polymers in most cases contain other non-polymeric additives: plasticizers to make them softer, reinforcements and fillers to improve mechanical properties such as stiffness and strength. Also, stabilizers and antioxidants are often necessary to protect them against ageing, light and biological agents. Often synthetic polymers are not biodegradable, their resistance against environmental degradation is very good. Therefore, recycling, although cumbersome and expensive, will remain an important issue. Polymers do not conduct electricity and heat well, which makes them ideal materials for electrical and thermal insulation. In general, polymers are tough materials, only a minority are brittle. Polymers usually do not resist heat very well and many loose their shape with increasing temperature. On exposure to air and water polymers remain pretty much unchanged. However, polymers can burn and then often emit soot particles and a variety of noxious gasses. Polymers are divided into three large groups: thermoplastics, thermosets, and elastomers or rubbers.

Thermoplastics

Thermoplastics consist of long chain molecules built up of small repeat units, called monomers. Polyolefines, with polyethylene (monomer: ethylene) and polypropylene (monomer: propylene) as main representatives, are long-chain hydrocarbons. The polyolefines are partly crystalline, therefore opaque (*i.e.* not transparent), and they are so light that they float on water. Polypropylene is widely used in consumer products, polyethylene mainly in packaging: bottles, bags and foils. Vinyl polymers have carbon chains to which, besides hydrogen, other side groups are attached. Well-known examples are polystyrene (PS), polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA, perspex, one of the most transparent plastics). PS is utilized in consumer products, PVC in large amounts in piping and, plasticized, in floor and furniture coverings. The so-called condensation polymers contain, besides carbon, other atoms like oxygen and nitrogen in the main chain. The nylons (fibres!) belong to this class as well as polycarbonate (tough and transparent) and polyethylene terephtalate (PET, for bottles and fibres). Liquid crystalline polymers (LCPs) are composed of rod-like, rigid molecules. These molecules can easily be aligned in the liquid state and retain their orientation in the solid state. This produces very stiff and strong materials with a high thermal stability. A good example are the aramids, used for strong, high-modulus fibres. Around 1955 it was discovered that a relatively easy way to produce new polymer materials was to combine two or more different polymers in a so-called polymer blend. In this way the favourable properties of the constituents may be combined. The first and still important example of a blend was high impact polystyrene (HIPS), where polystyrene, a brittle polymer, was blended with a small amount of rubber. Another way of combining polymers is copolymerization, where two or more different monomer types are incorporated in the chains. An example of a widely used copolymer is ABS (acrylonitrile–butadiene–styrene), a tough material for use in consumer products. Thermoplastics soften or melt when heated to moderate temperatures and harden when cooled. They are capable of being moulded and remoulded repeatedly, which allows easy processing and recycling.

Thermosets

In thermosets, the long chain molecules are arranged as a dense molecular network. These networks are formed during processing by a chemical reaction between the components, the prepolymer and a curing agent. As a rule, thermosets are much more brittle than thermoplastics. Therefore most thermosets contain large amounts (up to 60%) of fillers and/or reinforcements: mineral or organic particles, inorganic or organic fibres, *etc*. The thermoset product remains solid on heating, until finally chemical decomposition occurs. Applications are found in cases where resistance to heat and dimensional stability are important. The history of thermosets goes back as far as 1907 when Leo Baekeland invented Bakelite® (phenol formaldehyde resin, PF), which meant a revolution in the production of electrical fittings. Later other formaldehyde-based thermosets were developed: urea formaldehyde (UF) around 1930 and melamine formaldehyde (MF) in 1940. These have the advantage of a light colour, contrary to PF. They are still widely used, for example MF in decorative laminate sheets (Formica®, originally developed as a substitute for the mineral mica: ‘for mica’). Modern thermosetting materials include alkyds, polyesters, epoxies, polyurethanes and silicones. Alkyds form an essential ingredient of modern paints and coatings. Polyester thermosets are used in glass fibre-reinforced yachts and housings of electrical switches. A well-known example of application of epoxies is in high-performance adhesives. Polyurethanes are best known for foams, hard foams for building and insulation purposes, rubbery foams for mattresses. Silicones are applied as sealants.

Rubbers

Rubbers also consist of a molecular network in the finished product. The network in a rubber is, however, much less dense than in a thermoset. Similar to thermoplastics, rubbers have long chain molecules, but to prevent plastic flow during mechanical loading very localized bridges or cross-links are introduced to chemically connect these chains. The traditional process to do this is called vulcanization, where the cross-links are formed by sulphur atoms. This process was accidentally discovered by Charles Goodyear in the first half of the 19th century in his attempt to eliminate the stickiness of natural rubber by dusting it with sulphur powder and heating it. Nowadays also other vulcanizing agents are used and other, synthetic rubbers have taken over a great part of the market. The most important synthetic rubbers are copolymers of butadiene and small amounts of styrene or acrylonitrile: SBR and NBR. Car and bicycle tyres, gas hosing, seals, gaskets and conveyor belts are important applications of these rubbers. Silicone rubbers are synthetic specialty rubbers with an excellent resistance to high and low temperatures. They are chemically inert in almost all environments, which makes them very suited for insulation, sealants and medical applications (tubing, implants). In addition the general class of rubbers now also contains flexible thermoplastic materials that make use of physical cross-linking mechanisms, like crystallization and local phase separation, to form the required network. These thermoplastic elastomers (TPEs) have the advantage that upon heating the physical cross-links disappear by *e.g.* melting. Therefore, they may be processed by conventional thermoplastic processing methods.

1.3 Ceramics

The earth's crust is the source for the raw materials for ceramics. Ceramics are solids and usually are highly crystalline. However, in some cases glasses, which are non-crystalline or amorphous solids, can be formed. Ceramics often are combinations of metals and non-metallic elements. Typical ceramic compounds are the metal oxides, nitrides, borides and sulphides. The compounds composed of only non-metals such as silicon nitride and carbon nitride are also regarded as ceramics, as well as diamond and silicon. Normally ceramics are rather brittle, but in practice toughness can also be obtained. The variation in the strength of ceramics is surprisingly large and the production route primarily determines their properties. As a rule, ceramics are hard, strong, and wear and corrosion resistant when exposed to a wide range of environments. The physical properties of ceramics, like the conduction of heat and electricity, and their colour and refractive index, show large variations. This correspondingly leads to a wide range of opportunities for application. From an application point of view it is necessary to distinguish between structural and functional ceramics.

1.3.1 Structural ceramics

Mechanical loading is characteristic for parts made of structural ceramics. Strength and wear resistance are important. Well-known examples are roof tiles, bathroom products and modern kitchen equipment. Imperfections during production may lead to decreased resistance to mechanical loading. Therefore, products made of structural ceramics often have larger dimensions than strictly necessary. Furthermore, many structural ceramic products have a very traditional design. Both factors contribute to the high weight of the traditional toilet bowl!

Aluminosilicates

Classical ceramics (see Table 1.4.) are also called *triaxial* ceramics. Three ingredients, silicon oxide + clay + feldspar, are mixed with water yielding a plastic paste. Silicon oxide is also called quartz or sand. Clay and feldspar are mixed oxides containing aluminium oxide, silicon oxide and a range of other metal oxides, especially of sodium, potassium, magnesium and calcium. Quartz powder is a filling agent, clay and water make the mixture plastic and feldspar gives an increase of density. The properties of classical ceramics in products like teacups, bricks, tiles, and roof tiling, are predominantly determined by the ratio of the triaxial components and the processing temperatures. The secret of the porcelain process lies in the precise control of temperature and composition.

Cement

Processing of cement takes place at room temperature. Three categories of cement can be distinguished: hydraulic cement, condensation cement and acid-base cement. Hydraulic cement hardens by hydration *i.e.* the incorporation of water. Condensation cement hardens by water loss resulting from a polymerization reaction yielding a silica gel. Acid-base cement is a combination of a base-forming oxide like calcium oxide, and an acid-forming oxide like phosphor pentoxide. The latter cements are used for medical applications.

Titanium nitride and zirconia

Titanium nitride has a very high hardness and wear resistance. Therefore it is applied in the cutting edges of metal cutting tools. Titanium nitride has an attractive appearance: a very common steel watch obtains a golden appearance by applying a coating of titanium nitride, which also provides resistance to scratches and corrosion. Such ceramic coatings show how designers and engineers can combine the advantageous properties of steel (deformability) with the advantageous properties of titanium nitride (colour and durability) without the disadvantageous properties: rust and brittleness. In many cases, classical ceramics are too brittle for engineering applications. Toughness is often related to the possibility of energy dissipation. Some zirconias can dissipate energy by changing the atomic arrangement in the crystal. For instance, a ceramic kitchen knife should be very sharp but it must also possess a certain level of toughness when it hits the bone of a chicken during carving.

1.3.2 Functional ceramics

Parts made of functional ceramics always have special physical properties, *e.g.* conduction of heat or electricity, magnetism, optical properties (colour, refraction and luminescence), heat resistance and catalytic properties. The old-fashioned ceramic parts in lamp fittings and high-voltage insulation in spark plugs and X-ray tubes are good examples.

Glass ceramics

Glass ceramics combine the forming of glass with the processing of ceramics. Glass is a non-crystalline or amorphous solid. Glass ceramics are obtained by the following route: after the forming of the product a special heat treatment is given during which the non-crystalline solid transforms into a crystalline solid. Glass ceramics commonly have a very low coefficient of thermal expansion leading to applications like ceramic induction plates for the kitchen.

Alumina and diamond

Alumina is aluminium oxide, it has a high melting temperature of about 2000ºC. Sapphire and ruby are different forms of aluminium oxide, their colour is determined by the presence of other trace elements like chromium or nickel. The yellow sodium lamps used for motorways have an inner coating of alumina: it is transparent for the emitted light and resistant to the highly reactive sodium vapour inside these lamps. Alumina is used for high-voltage insulators and in temperature resistant parts for the chemical industry. Diamond has the highest hardness of all known substances. Hence, a diamond tool can cut any other substance. Diamond is an electric insulator, but a good conductor of heat. At room temperature, diamond is very inert, but at high temperatures it can even burn (diamond is a form of carbon). Under special conditions, diamond coatings can be made by chemical vapour deposition. These coatings can enhance biological acceptance of prostheses or provide high surface durability.

Glass fibres and germanium dioxide

Telecommunication is the conveying of information by electromagnetic radiation. The transport capacity depends on the frequency of the used radiation. Light has a much higher frequency than the electric signals in the traditional copper telephone cables. As pure glass is transparent, glass fibres can be used for telecommunication over large distances. To keep the light inside the glass fibres a radius dependent content of germanium dioxide is used, giving rise to a gradient index fibre. In practice the loss of light is so small that the information can be transported over many (hundreds of) miles before requiring amplification.

Problem 1.2 *Which functional ceramics are discussed in the above paragraph?*

1.4 Biomaterials

Products derived from biological sources have been used for man's needs for tools, shelter and comfort since prehistoric times. Those biomaterials may originate from plants or animals and they are usually complex compositions of carbohydrates, proteins and numerous other metabolic products. Biomaterials are basically different from metals, synthetic polymers and ceramics as they are formed through metabolic pathways in living organisms, *e.g.* CO_2 fixation *via* photosynthesis in trees yields wood. Therefore, the resources of biomaterials are considered to be inexhaustible and renewable, in contrast to materials based upon fossil resources. Biomaterials sometimes can be obtained in pure form, but mostly will require refining and extraction before they can be applied in functional products. Biomaterials appear in a wide variety of forms and properties, ranging from lightweight hollow bamboo pipes to high-density hard woods, from highly elastic rubbers to thin flexible paper sheets. Since all biomaterials in principle are (bio)degradable, protection against premature deterioration is required in many applications.

Wood and cellulose

Forestry provides wood for the construction of wooden buildings and houses, furniture and tools. Besides, wood is used as fuel. Wood is composed of fibre cells that are built up of cellulose fibrils glued together by lignin and hemicellulosic polysaccharides. Many wood species are suitable for use as timber, ranging from single use items (such as crates) to durable woodcarvings and works of art. Depending on the species, wood properties may be very different, finding accordingly other end uses. Lightweight wood types, like balsa wood, find application in (model) aeroplanes, certain tropical hardwoods (meranti, merbau) with a homogeneous grain are favoured for window frames. Ash wood typically is used in handles of tools (hammers) and broomsticks, and oak furniture is highly appreciated due to its high quality. Cellulose is extracted on a large scale from wood and other plant materials by a combined chemical and thermomechanical pulping process, often for paper production. Besides paper production, cellulose pulps are applied to produce cardboard and corrugated board for boxes, tubes and wrapping paper, widely used in packaging. Cellulose pulp can be transformed into many shapes and 3D forms (*papier mâché*) by dehydration. Cellulose-based products in general are moisture sensitive and require protection if prolonged use and durability is desired.

Rubbers

Natural rubber latex is tapped from the wounds made in the bark of the rubber tree. It consists of isoprene-based polymer chains that can be cross-linked by a process called vulcanization. The high extensibility and impact resistance are unique properties that have given rubber a major position in the manufacture of elastic products, ranging from stopcocks, rings, belts to gloves and condoms. Besides, natural rubbers find application in large tyres for trucks, lorries and aeroplanes, as they show a lower heat generation during use than synthetic rubbers.

Thermoplastics and thermosets

The thermoplastic processing of carbohydrate polymers such as starch can be performed if precautions are taken to prevent dehydration and by adding suitable plasticizers. Because of the water sensitivity and biodegradability, starch-based plastics are largely used for single-use products (trays, packaging foils). Blends with polyester have been marketed for use in compostable plastic bags. Natural monomers are the renewable resources for the production of thermoplastic polyesters. Examples are polylactic acid and polyhydroxyalkanoate, which are obtained by fermentation processes. Because these polymers still are relatively expensive, they are applied in special niche products, such as medical implants, which can be dissolved by the body after some time, saving the necessity for a second operation for removal. Another group of thermoplastic biopolymers are cellulose derivatives, such as cellulose diacetate, that can be processed into a broad range of products from foams (cigarette filters) to transparent plastic foils and solid glass-like products. Various biopolymers show irreversible cross-linking upon heating, yielding thermosetting biopolymers. Typical examples are proteins and phenolic plant components (lignin), but also semi-synthetic products such as furan (furfural resins) or alkyd-based resins, which are commercially used in coatings and adhesives.

(Textile) fibres

Cellulose plant fibres such as cotton, flax, hemp and jute find wide application in textiles, such as fabrics for clothing and upholstery. Cotton is mainly used for clothing, while jute is traditionally used in bags for packaging of agricultural products. Coarser fibres such as sisal and coir (coconut fibre) find application in ropes, brushes and doormats. Animal-derived fibres such as wool and silk are based upon proteins. Wool is commonly used in clothing industries to produce sweaters, but also for floor covering. Silk is used only in very delicate fabrics such as shawls and blouses. Many of the natural fibres can be found in blended yarns with other (man-made) fibres, such as polyester and acrylic fibres.

Composites

Many products, which are partly or completely based upon renewable raw materials, come in the form of a composite. Typical examples are linoleum (linseed oil and wood flour), and fibre boards (medium and high density fibre boards MDF and HDF, plywood, particle board), commonly based upon processed wood with urea or phenolic resin as a binder. These are widely used in building panels and furniture, table blades and kitchens. Natural fibre reinforced composite materials (hemp, flax, jute) are produced by injection moulding or sheet moulding processes, for use in lightweight indoor car panels, replacing glass fibre compounds.

Leather and other biomaterials

Leather produced from animal hides is favoured for the production of shoes and belts, but finds many more uses in, for example, furniture, coats, purses and leather bags. The skins require preparation by chemical treatment (tanning). Numerous other materials derived from plant or animal sources have been applied for specific purposes, such as cork, mainly known as stopper on wine bottles, but also finding use in floor covering, insulation, shoes (soles), and life jackets. Another example, finding yet limited application, is chitin and its derivatives, which are extracted from the outer shells of crabs, lobsters and shrimps, as a residue from the seafood industry. Because of relatively high costs of production chitin finds application in high added value products such as medicinal bandages and cosmetic products such as toothpaste, as well as filters, coatings and adhesives.

Chapter 2

Properties and testing

2.1 Introduction

A tree is known by its fruit. Similarly, products are designed to perform certain desired functions. The performance of the product is related to the underlying material properties, the production process and, of course, the design. The ‘fruit’ of a material are its properties. A material property is any aspect of the material that links a material with functional or processing requirements. The following may serve as an example. Suppose, the product is a bar used to convey a certain tensile force. Then, the ultimate force per unit of cross-section that the bar can withstand is a relevant property. This property is called strength. This link between material properties and requirements of the product may seem obvious, and indeed often is. However, there is no general theory to connect properties and performance. In each design, the designer and the engineer have to examine what essential functions the product has to fulfil and which material properties are then required.

Many material properties can be measured and expressed quantitatively. However, some can only be observed by one of the senses and described qualitatively, *e.g.* colour, touch and smell. As said previously, some properties of substances and materials are related to functional requirements, others are related to their processing. Sometimes such properties are called the ‘abilities’. Examples are the weldability, the castability and the machinability. This chapter does not deal with these abilities. Some of the factors concerning the processing of materials will be discussed later in this book (see Chapter 10).

As stated before, the designer and the engineer should be focused on that combination of properties that copes with the essential functional product requirements. Hence, to a large extent design and engineering can be traced back to the link between material properties and functional requirements. Table 2.1 gathers the properties frequently encountered in design and engineering (see Ashby (2005)).

Table 2.1. Most important material properties.

	property	*symbol and unit*
general	price	€, $
	density	ρ [kg/m^3]
mechanical	elastic moduli	E,G,K [GPa]
	strength	σ_f [MPa]
	fracture toughness	K_c [MPa.m$^{1/2}$]
thermal	conductivity	λ [W/(m.K)]
	diffusivity	a [m^2/s]
	specific heat	c_p,c_v [J/(kg.K)]
	melting point	T_m [K]
	coefficient of thermal expansion	α [1/K]
wear	Archard wear coefficient	K_A [1/MPa]

2.2 Properties and their relations

2.2.1 *Elasticity and strength*

The following loading modes are important for the designer and engineer: tension/compression, shear/torsion and hydrostatic pressure. Compression loading is often important in architecture. Shear in torsion depends on the distance from the torsion axis. As long as the deformations, *i.e.* strains, for the loading modes indicated are completely reversible, these deformations are called elastic. To first approximation the strains are proportional to the applied stresses. The elastic moduli are then defined as the constants relating stresses and strains for the loading modes indicated. The constant for tension/compression is called the Young's modulus E. In the remaining part of this book the Young's modulus will be called the E-modulus. For shear and torsion we use the shear modulus G and for hydrostatic compression the bulk modulus K. In case of a uniaxial tensile stress, the strain in the axial direction is positive whereas the strain in the transverse direction is negative.

When a metal bar is loaded in tension, the relation between the applied strain ε and stress σ is given by Figure 2.1. The strain ε is given by the variation of the length divided by the original length $\Delta l/l_0$ and the stress σ is the load F divided by the original cross-section A_0. Then, the E-modulus can be defined as the derivative or slope of the stress-strain curve at the origin.

The ratio between the transverse and the axial strain is called Poisson's ratio, which is defined as a positive number: $\nu = -\varepsilon_{trans}/\varepsilon_{long}$. For most materials the value of Poisson's ratio lies between 0.2 and 0.5.

Problem 2.1 *Show for an elastic elongation at a constant volume that the value of Poisson's ratio equals 0.5.*

Problem 2.2 *If the value of Poisson's ratio lies between 0.2 and 0.5 and a tensile test specimen is subjected to a uniform elastic elongation, does its volume increase or decrease?*

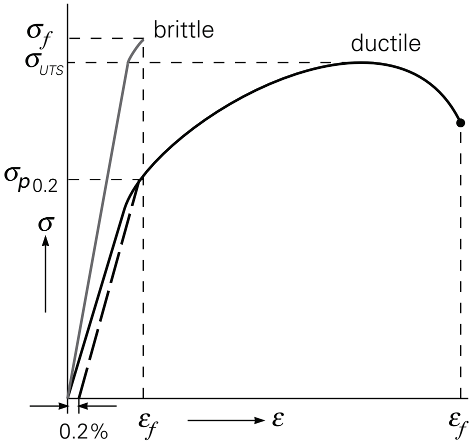


Figure 2.1. Schematic stress-strain curve for a brittle and a ductile material.

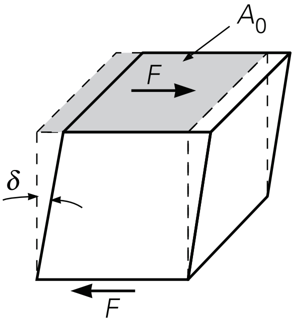


Figure 2.2. Shear γ (with $\gamma = \tan\delta$) resulting from a force on a given area.

The shear stress τ follows from the shear load F divided by the area of shear A_0. As long as the deformation applied is fully elastic, the shear modulus G is given by the shear stress τ divided by the shear γ (see Figure 2.2). When a hydrostatic pressure P is applied to a specimen so that the volume V changes elastically by an amount ΔV, the bulk modulus K is defined by $P = K\,\Delta V/V$. Isotropic materials show the same properties in all directions. In this textbook, all materials are assumed to be isotropic unless indicated otherwise. For an isotropic material holds:

$$E = 3K(1-2\nu) \quad \text{and} \quad G = \frac{3K\,(1-2\nu)}{2\,(1+\nu)} \tag{2.1}$$

The engineering strength can be regarded as the safe loading divided by the cross-section on which the force is acting. So, strength has the dimension of stress. This engineering strength cannot be defined unequivocally, as it may depend on the constraints on the allowed deformation for a certain application. For metals and alloys, the engineering stress is usually taken as the stress at a certain permanent deformation, mostly 0.2% in tension: $\sigma_{p0.2}$ (see Figure 2.1), this is commonly called the yield stress, σ_y. A permanent deformation is non-elastic by nature and is known as plastic deformation. For polymers, the yield stress is normally taken at 1% of permanent deformation. After continued plastic deformation, finally fracture occurs. The tensile strength (denoted as σ_{UTS}, σ_m or σ_t) is the stress at the maximum of the stress-strain curve. For metals and alloys the value of σ_{UTS} is larger than $\sigma_y = \sigma_{p0.2}$ (see also Section 2.3). For ceramics, which fracture in a brittle way without preceding plastic deformation (see Figure 2.1, dashed curve), the strength depends strongly on the loading mode. In tension, the engineering strength is equal to the fracture strength $\sigma_f^{\,t}$. In compression, the engineering strength is denoted as crushing strength $\sigma_f^{\,c}$:

$$\sigma_f^c = 15\sigma_f^t \tag{2.2}$$

Finally, the hardness H can be related to strength, where the following rule of thumb often holds:

$$H = \tfrac{1}{3}\sigma_f \tag{2.3}$$

2.2.2 Fracture toughness

In virtually all products very small, microscopic flaws or cracks are always present at the surface and within the interior of the material, and/or are formed under stress (Figure 2.3). These flaws are detrimental, since at the tips of a crack stress concentration occurs: the local stresses are higher than the nominal applied stress. Note that stress amplification and concentration also arises at sharp corners and edges, notches and voids, making these also susceptible to crack formation and failure.

The study of fracture mechanics was initiated during World War I by the English aeronautical engineer A.A. Griffith. Griffith's work was motivated by the fact that the stress needed to fracture bulk glass is around 100 times lower than the theoretical value. Crack formation and growth in a perfectly brittle material proceeds without any plastic deformation and only implies the formation of two new surfaces and an increase in surface energy γ_s [J/m^2]. On the other hand, the crack relaxes the stress, thereby reducing the elastic energy near the crack, a process that is governed by the E-modulus. Together this leads to Griffith's equation for the critical local stress σ_c at which a crack of length $2a$ will propagate and will lead to fracture:

$$\sigma_c = \sqrt{\frac{2E\gamma_s}{\pi a}} \tag{2.4}$$

Problem 2.3 *Rearrangement of Equation (2.4) gives* $\sigma_c\sqrt{a} = \sqrt{2E\gamma_s / \pi}$ *. The right hand side of the latter equation only contains material properties. As a result* $\sigma_c\sqrt{a} = C$ *, a constant for a given material.*

In order to test his theory Griffith carried out fracture tests on precracked cylindrical tubes of 'hard English glass'. In the Table below some of his experiments are shown:

$2a$ [*inches*]	σ_c [*lbs. per square inch*]
0.25	678
0.30	616
0.38	526

Check that Griffith's theory is correct in so far that C is indeed a constant.

However, Equation (2.4) applies only to perfectly brittle materials. For all other materials the work required to create new crack surface is more than just the surface energy. Other energy-absorbing processes, especially plastic deformation in the vicinity of the crack tips, need to be included. These were taken into account by G.R. Irwin in the 1940s by replacing the surface energy term in Griffith's equation by the *toughness* G_c, also known as the *critical strain energy release rate*:

$$\sigma_c = \sqrt{\frac{EG_c}{\pi a}} \tag{2.5}$$

with $G_c = 2\gamma_s + G_p$ (2.6)

where G_p is the plastic dissipation per unit area of crack growth. For an almost ideally brittle material like glass $G_c = 2\gamma_s$, for nearly all other materials the plastic dissipation term dominates and $G_c \approx G_p$.

Later, in the 1950s, Irwin showed that the energy approach, leading to G_c, is equivalent to an approach based on the stress amplification at the crack tip. The material property which governs the process of crack propagation and fracture is called the *fracture toughness* K_c. It is related to G_c by $K_c = \sqrt{EG_c}$.

Samples can be loaded in different modes. Mode I, the tensile mode, is the condition in which the crack plane is normal to the direction of the stress, as is the case in Figure 2.3. Mode II, the sliding mode, involves shear and Mode III, the tearing mode, involves torsion.

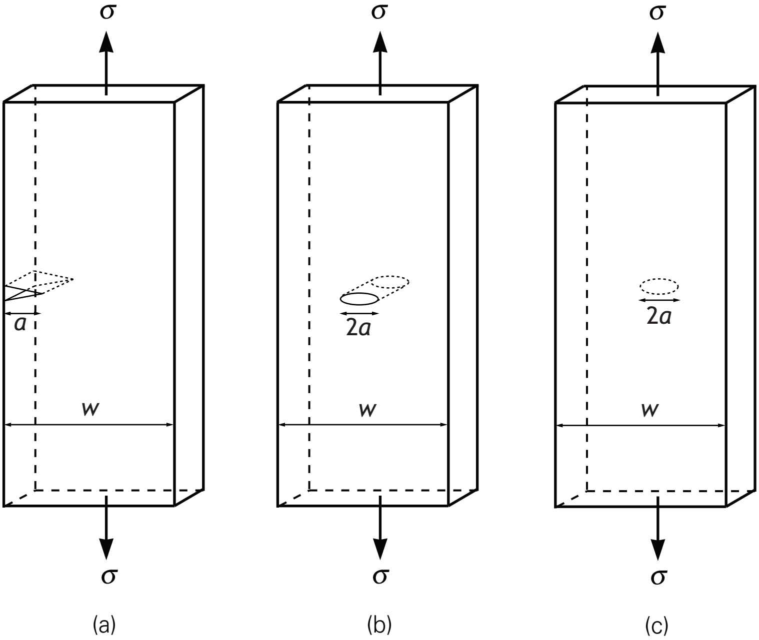


Figure 2.3. Cracks in a plate of semi-infinite width (w ≫ a): (a) edge crack; (b) interior through-thickness crack; (c) interior embedded crack.

The most commonly encountered mode in practice is the tensile mode:

$$K_{Ic} = Y\sigma_c\sqrt{\pi a} \tag{2.7}$$

A dimensionless parameter Y is introduced to account for different crack geometries (see Figure 2.3), and crack and specimen sizes. For an interior through-thickness crack (b) $Y = 1$, for a through-thickness edge crack (a) $Y = 1.12$ and for an embedded crack (c) Y varies between $2/\pi$ (circular crack) and 1 (elliptical crack with a mayor diameter much greater than the minor diameter). These values are only valid when the cracks are much smaller then the width of the specimen ($a \ll w$ in Figure 2.3).

Problem 2.4 *Which is more detrimental for the strength of a material, an edge crack, an interior through-thickness crack or an embedded crack, all of the same length?*

As mentioned before, the fracture toughness is lowest for brittle materials like ceramics and glassy polymers and high for ductile materials like most metals. In Table 2.2. values of K_{Ic} for some materials are given.

Table 2.2. Typical values of the plain strain fracture toughness for selected engineering materials at room temperature.

material	K_{Ic} [MPa.m$^{1/2}$]
soda-lime glass	0.7
marble	1.0
granite	1.5
concrete	0.2 – 1.4
polystyrene	0.7 – 1.1
polymethyl methacrylate	0.7 – 1.6
polycarbonate	2.2
high-density polyethylene	1.1 – 1.5
low-density polyethylene	1.0 – 1.1
nylon	1.2
mild steel	140
alloy steel	50 – 90
aluminium	14 – 28
aluminium alloys	24 – 45
titanium alloy	44 – 60

Problem 2.5 *1. How high is the critical stress for a glass specimen in tension when the largest cracks are in the order of 0.5 mm? Assume a value of 1.0 for Y.*

2. What would be the critical stress if glass is an ideally brittle material? The surface tension of glass is 1 J/m^2 and its modulus 70 GPa.

2.2.3 Density, heat and wear

The density ρ is the mass per unit volume. The relative density is the density divided by the density of water. With increasing temperature a substance will expand; the length l of a bar will grow according to $\Delta l = \alpha \, \Delta T \, l$, where α denotes the linear thermal expansion coefficient and T the temperature. For an isotropic material, the volume thermal expansion coefficient is equal to three times the linear thermal expansion coefficient. A solid conducts heat. The conduction of heat between an area at temperature T_1 and an area at temperature T_2 is determined by the thermal conductivity λ. The heat flow is given by:

$$q = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x} \left(= \frac{\lambda\,(T_1 - T_2)}{\Delta x} \quad \text{if linear temperature profile} \right) \tag{2.8}$$

with $T_1 > T_2$ and Δx = distance between area at T_1 and area at T_2.

Suppose an external thermal source is heating a piece of material. The heat diffusion in that material can be described by the thermal diffusity a:

$$a = \frac{\lambda}{\rho\, c_p} \tag{2.9}$$

The value of a is very small for polymers, which has important technological and economical implications: after processing at elevated temperatures rather long cooling times are necessary. On the other hand, this low value implies good heat insulating properties that are an important asset for a wide range of applications.

Wear is difficult to describe quantitatively. Wear occurs when two surfaces glide over each other. This results in a loss of material that depends on the pressure P perpendicular to the sliding surfaces, caused by the force F. The lost volume from one surface per unit sliding distance, L_s, is the wear V_w. The wear resistance of the surface A with perpendicular pressure P is characterized by the Archard wear coefficient K_A:

$$K_A = \frac{V_w}{P\,A} = \frac{V_w}{F\,L_s} \tag{2.10}$$

2.2.4 Interrelations of intrinsic properties

The properties so far all meet the definition given for a property: *a material property is any aspect of the material that links a material with functional or processing requirements*. Matter contains space, atoms and electrons. Properties that are related with the behaviour of atoms and electrons are called *intrinsic* or *fundamental* properties. An example is the coefficient of thermal expansion. On the other hand, properties primarily depending on the extent and/or composition of the assemblies of atoms are called the *extrinsic* properties. An example of the latter is the strength of a metal alloy that depends on composition but also on grain size (see Section 3.3.3). Considering their origin, it can be expected that the intrinsic properties are interrelated. This is illustrated below for some thermal and mechanical properties.

Thermal expansion implies an increase in volume. The atoms of a material vibrate and the amplitude of the thermal vibrations increases with temperature. The relation between the change of vibration frequency and the volume resulting from the temperature increase is given by Grüneisen's constant γ_G. The value of this constant is between 0.4 and 4, but for most solids the value lies between 1 and 2 (see Ashby (2005)). For the coefficient of linear thermal expansion can be derived (see also Cottrell (1964)):

$$\alpha = \frac{\gamma_G \rho c_v}{3E} \tag{2.11}$$

According to this equation, the coefficient of thermal expansion is inversely proportional to the value of the elastic constants (see Equation (2.1)). For solids, the specific heat at constant volume, c_v, is nearly equal to the specific heat at constant pressure, c_p, although the difference between the two tends to increase with increasing temperature. To first approximation, it holds for a large range of temperatures that the value of the specific heat is independent of the temperature. It is found that the specific heat is related to the mass of the atoms and that the product of density and specific heat can be assumed to be constant. For many solids it is found that (Ashby (2005)):

$$\rho c_v = \rho c_p = 3 \cdot 10^6 \ \ [\mathrm{J/(m^3K)}] \tag{2.12}$$

To first approximation (Ashby (2005)), the elastic constants are proportional to the melting point T_m in K:

$$E = 100 \cdot 10^6 \, T_m \tag{2.13}$$

Then, it follows *via* Equation (2.11) that the coefficient of thermal expansion is inversely proportional to the melting point:

$$\alpha = \frac{\gamma_G}{100 \, T_m} \tag{2.14}$$

Problem 2.6 *Compare the coefficient of thermal expansion for aluminium with the one for iron using Equation (2.14).*

With Equations (2.9) and (2.12), the *thermal diffusivity* for many solids can be written as:

$$a = \frac{\lambda}{3 \cdot 10^6} \tag{2.15}$$

Some solids deviate from the rule indicated by Equation (2.15). The largest deviations are found for porous solids, like foams.

2.3 Mechanical testing

2.3.1 The tensile test

The tensile test is by far the most important method of mechanical testing. Standard tensile test specimens are strained under standard conditions until fracture occurs. The relation between force and imposed elongation is continuously recorded. The measured force is divided by the original cross-section of the test specimen.

This calculated stress is recorded as a function of the strain, which is the imposed elongation divided by the original length of the test specimen (see Figure 2.4).

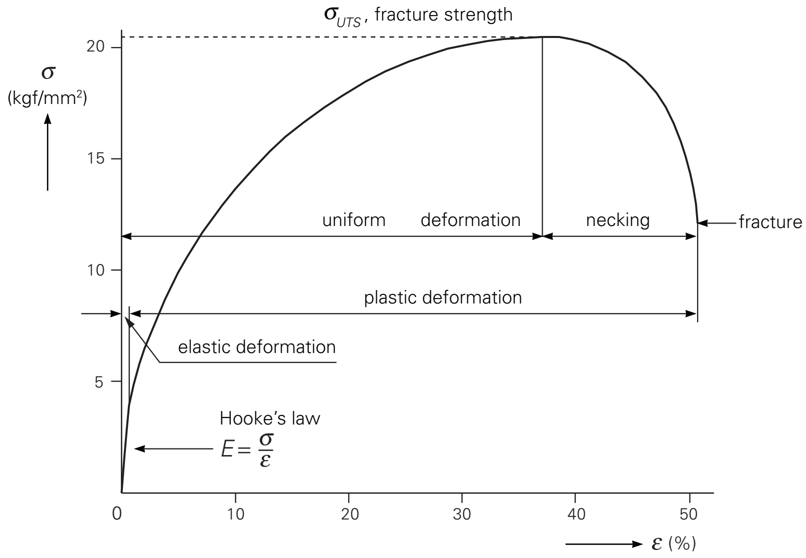


Figure 2.4. Stress-strain curve for annealed copper (Brandsma et al. (1960)).

The stress-strain curve for metals will be discussed on the basis of this Figure. For small elongations (see also Section 2.2.1) there is a linear relation between the strain ε and the tensile stress σ:

$$\sigma = E\varepsilon \qquad \text{with } \varepsilon = \Delta l / l_0 \tag{2.16}$$

Equation (2.16) is known as Hooke's law and only holds for small strains. Further elongation might be elastic, but not necessarily linearly elastic. The upper stress limit for the validity of Hooke's law is called the proportionality limit. Below the elastic limit total recovery of the specimen shape occurs after removing the strain. The elastic limit is just above the proportionality limit. Above the limit of elasticity, permanent strain occurs: the deformation becomes *plastic*.

On performing the tensile test, the standard specimen starts to elongate without any shape change of the perpendicular cross-section, this is called uniform elongation. For the large majority of experiments, the recorded force on prolonged elongation starts to decrease quite suddenly. Mostly just halfway the length of the standard tensile test specimen, the cross-sectional area starts to decrease: necking occurs. As the recorded force is divided by the original cross-section area, the calculated stress decreases strongly. The maximum observed stress is called the ultimate tensile stress. The following symbols can be encountered for this maximum: σ_{UTS}, σ_m, σ_t, R_{UTS}, R_m. After necking, finally fracture of the specimen occurs. The differences between the limits of proportionality and elasticity are generally difficult to determine experimentally. For designers and engineers the stress value corresponding to the onset of plastic strain is of course very important. Therefore, the stress value at which a small amount of permanent or plastic strain occurs is taken as the strength and is called the yield strength (see Section 2.1):

$$\sigma_y = \sigma_{p0.2} \tag{2.17}$$

The above description is a general picture of the stress-strain curve for metals. Steel is in many ways a special case. Steel is here taken as a common name for alloys of iron and very small amounts of carbon (see for the concept of an alloy, Chapter 4 and for steel in particular, Chapter 5). When applying a small elongation on a steel tensile test bar, the recorded force (and hence the calculated stress) increases quite strongly, indicating a large value of the E-modulus. Suddenly, at the onset of plastic deformation, the stress decreases and starts oscillating around a certain level. This is called the flow of steel or the yield point phenomenon. At a certain, higher strain the recorded force starts to increase again. The upper limit of the calculated stress at the flow start is called the upper yield point, σ_{eU} and the lower value during flow is called the lower yield point, σ_{eL} (see Figure 2.5). It is often assumed that steel obeys Hooke's law until the upper yield point. The yield strength of steel is normally taken as:

$$\sigma_y = \sigma_{eL} \tag{2.18}$$

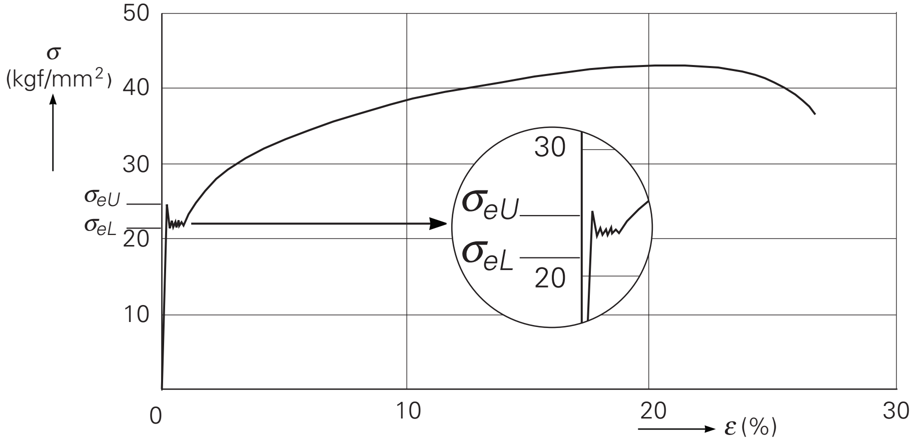


Figure 2.5. Stress-strain curve for steel (Brandsma et al. (1960)).

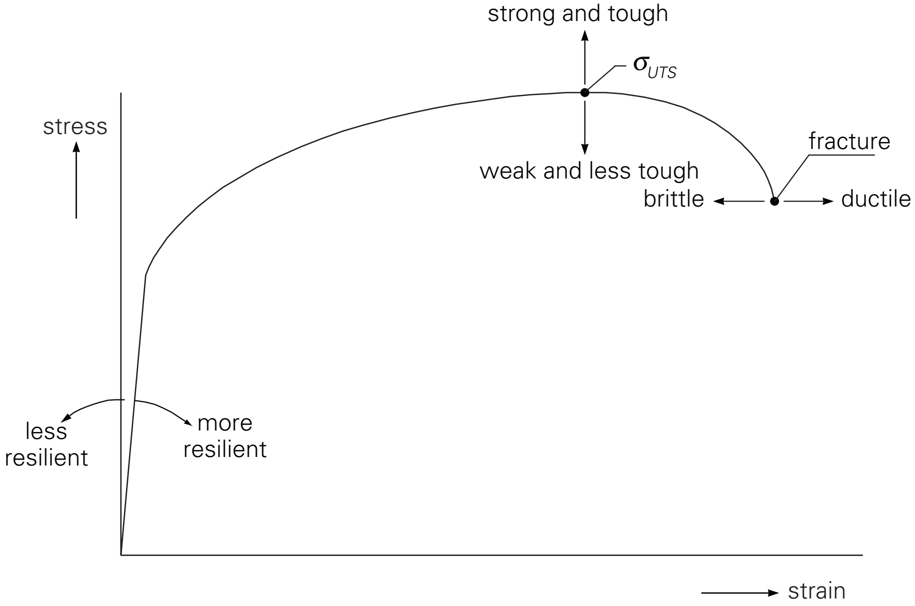


Figure 2.6. Terminology of the mechanical behaviour of metals (Brandsma et al. (1960)). Note: a tough metal shows both strength and ductility.

The stress-strain curve as described can serve to define some common terms also used by the materials scientist (see Figure 2.6). A metal with a higher value for the E-modulus can be denoted as ‘stiffer’. However, it should be noted that stiffness as such is a characteristic of a construction or a product. The stiffness of a structure results from *both* the value of the E-modulus of the material and its shape. It is obvious that engineers and designers play a major role in determining the shape of a construction or a product.

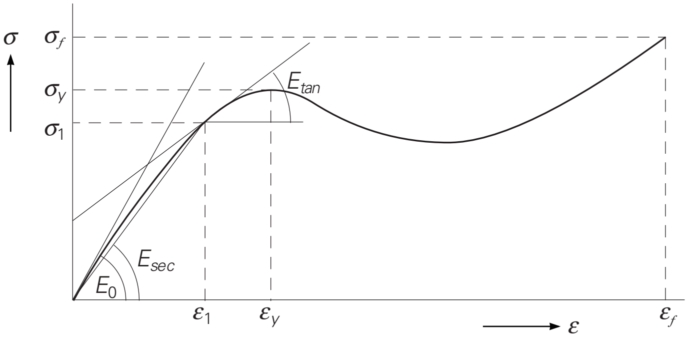


Figure 2.7. A schematic stress-strain curve for polymers.

A schematic stress-strain or σ-ε curve for thermoplastic polymers is shown in Figure 2.7. From such a curve can be derived: the E-modulus, the yield stress σ_y and the fracture stress or ultimate tensile stress, σ_f or σ_{UTS}. If the first part of the σ-ε curve obeys Hooke's law, *i.e.* if σ is linearly dependent on ε, then the E-modulus is given by $E = \sigma/\varepsilon$. However, if the curve is non-linear from the start, the E-modulus has to be calculated from:

$$E_0 = \left(\frac{d\sigma}{d\varepsilon}\right)_{\varepsilon=0} \tag{2.19}$$

The E-modulus of a polymer is usually taken as this *initial* value, also denoted as the *short-term* modulus. Creep is the continuous elongation under constant loading. Creep is far more important for polymers than for metals (see also Chapter 7). During creep the value of the E-modulus taken as the ratio of applied stress and the time dependent strain will decrease as a function of time. In practice it is customary to define another E-modulus for larger values of strain. This can be done in two ways:

1. the secant modulus:

$$E_s = \frac{\sigma_1}{\varepsilon_1} \tag{2.20}$$

2. the tangent modulus:

$$E_t = \left(\frac{d\sigma}{d\varepsilon}\right)_{\varepsilon=\varepsilon_1} \tag{2.21}$$

Some polymers show a brittle fracture at a small strain of only a few %. Others are more ductile and exhibit flow at a certain stress level σ_y (see

Figure 2.8). The stress increases only slightly and sometimes even decreases a little. Actually, this stress can be regarded as the failure stress, although real fracture only occurs at a slightly higher stress, σ_f and a much larger strain ε_f. The integral area below the curve is the energy necessary for fracture. This amount of energy is a measure for the ductility of the tested material.

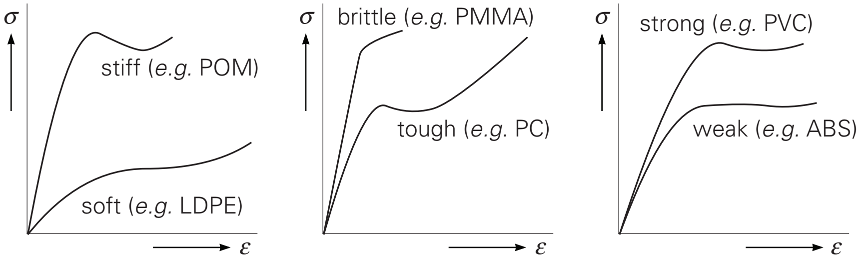


Figure 2.8. Typical examples of stress-strain curves of some polymers.

Problem 2.7 *Show that the area below the σ-ε curve has the dimension of energy per unit volume.*

Due to the imposed elongation the tensile test specimen becomes thinner. The uniform decrease of the cross-sectional area is called contraction. The reduction of the cross-sectional area implies that the recorded stress, *i.e.* the measured force divided by the area at the start of the tensile test, is not equal to the true stress in the test specimen. The true stress is given by:

$$\sigma_{tr} = \frac{F}{A} \tag{2.22}$$

where F = the actual force and A = the actual cross-sectional area. To first approximation it holds: $A \cdot l = A_0 \cdot l_0$.

Problem 2.8 *Derive the following equation: $\sigma_{tr} = \sigma_0\,(1+\varepsilon)$ with σ_0 = the recorded nominal stress during the tensile test.*

2.3.2 Hardness tests

For practical purposes it is often important to know with which substance it is possible to scratch into other materials. This property is called *hardness*. The hardness of a material is not a fundamental property, *i.e.* a property directly to be linked with the atomic structure of the material involved. In fact, hardness is almost impossible to define uniquely. As a result, different hardness tests have been developed in the course of time. The present hardness testing methods all start from the following description: *hardness is the resistance of a material to permanent indentation*.

The result of a hardness testing is expressed as a number, where the hardness of the material tested is compared to the hardness of other materials tested by the same method. As stated, the hardness testing methods have evolved over time. As a result, the units of hardness do not correspond to the modern units of measurement. As hardness is primarily considered as a relative value, this anomaly will probably remain.

Rockwell hardness

The depth of a forced indentation is a measure for the hardness of the tested specimen. In essence, the Rockwell test implies a measurement of a different level of indentation. The indentation body is pushed onto the specimen with an initial minor load of 10 kg corresponding to about 100 N in order to eliminate small imperfections of the specimen and/or apparatus. The measuring scale is set unto 100. Then, the major loading takes place and the indentation depth increases. The scale pointer moves to lower values. When it stops the major loading is removed while the minor load is maintained. The end value as indicated by the pointer is read as the Rockwell hardness. The lower the hardness, the lower the end values. Very soft specimens would give negative hardness values. In that case the starting value is taken equal to 130. It should be noted that Rockwell values obtained with this larger starting value cannot directly be compared with the other values. Specimens with very high hardness would give very small, nearly undetectable indentation depths. In such cases, the major load is increased and/or an indenter made of diamond is used. The standard indenter is a steel ball. When reporting the results of a Rockwell test it is necessary to state the experimental conditions applied (see. Table 2.3).

Table 2.3. Rockwell testing.

test	*indenter*	*minor load* [*kg*]	*major load* [*kg*]	*total* [*kg*]	*scale*
A	diamond	10	50	60	100
B	1/16” ball	10	90	100	130
C	diamond	10	140	150	100
D	diamond	10	90	100	100
E	1/8” ball	10	90	100	130
F	1/16” ball	10	50	60	130
G	1/16” ball	10	140	150	130
H	1/8” ball	10	50	60	130
K	1/8” ball	10	140	150	130

Problem 2.9 *The Rockwell test presumes a specimen and a measuring apparatus. Indicate where elastic deformation may occur.*

Brinell hardness

During the Brinell test a sphere with a diameter *D* performs an indentation as a result of a loading with a force *P*. After removal of the sphere, the diameter *d* of the indentation is measured. The Brinell test is not a differential measurement, like the Rockwell test. The value for the Brinell hardness follows from Equation (2.23):

$$HB = \frac{2P}{\pi D\{D-(D^2-d^2)^{1/2}\}} \tag{2.23}$$

The results of the calculations involved are gathered in tables. Brinell hardness values should always be given together with the relevant testing conditions (see Table 2.4).

Table 2.4. Brinell hardness tests.

thickness of specimen [*mm*]	*ball diameter D* [*mm*]	*load* [*kg*]				
		30 D^2	10 D^2	5 D^2	2.5 D^2	D^2
> 6	10	3000	1000	500	250	100
6 - 3	5	750	250	125	62.5	25
3 - 1	2.5	187.5	62.5	31.2	15.6	6.25
materials:		steel	brass	copper, aluminium	soft solder	lead

To first approximation it holds that the magnitude of the indentation depends on the load and the diameter of the sphere. For conformal indentations, it appears that the ratio P/D^2 is a constant for a certain material. Generally, the proportion between the diameter *d* expected and the diameter of the sphere *D* is chosen such that deviations from conformity can be neglected. The value of *d* is in general between 0.2 and 0.6 *D*. The result of this yields ratios P/D^2 as given by Table 2.4. On application of the ratios mentioned in Table 2.4, it can be expected that different materials with similar hardness will show similar Brinell hardness values.

Vickers and Knoop hardness

During the Vickers test a small diamond of pyramidal and standardized geometry is forced into the specimen. The applied loads are much smaller than those in the preceding tests: in the range of 1 to 1000 grams. As the diagonal *d* of the resulting impression is observed and measured microscopically, it is necessary to polish the specimen's surface quite carefully beforehand. The magnitude of the loading is chosen such that the microscopic measurement can be performed at a magnification of 100×. The Vickers hardness value follows from Equation (2.24):

$$HV = \frac{1.85\,P}{d^2} \tag{2.24}$$

The Knoop test differs from the Vickers test in geometry of the pyramid. The Vickers pyramid has a square base plane, while the Knoop pyramid has a rhombic base plane. The Knoop test is often used for ceramics. The obtained indentation is microscopically determined by measuring the length of the long diagonal. The Knoop hardness value follows from Equation (2.25):

$$HK = \frac{14.2\,P}{l^2} \tag{2.25}$$

Both Vickers and Knoop hardness values are gathered in tables as a function of the measured diagonal lengths.

An overview of current hardness testing techniques is given by Table 2.5. The Shore D test for polymers is further discussed in Section 7.3.2.

Table 2.5. An overview of different hardness testing techniques.

symbol	*name*	*indentation body*	*application*
HB	Brinell	steel or tungsten carbide ball (D = 10 mm)	metals, measurement after indentation
HV	Vickers	diamond pyramid	metals and polymers, measurement after indentation
	Shore D	steel cone with rounded tip (d = 0.1 mm)	polymers, measurement during indentation
HRx	Rockwell (x depends on indentation body and load)	diamond cone or steel balls of different diameters	nearly all metals and polymers, measurement mostly after indentation

Problem 2.10 *Characterize the hardness testing methods according to the following criteria: accuracy, representativity and reproducibility.*

2.3.3 Fracture and failure

A man-made construction should not fail. Unfortunately, all earthly things are imperfect and some knowledge of failure is important. Here, we restrict ourselves to failure under mechanical stresses and three forms of failure will be discussed briefly: fracture, creep and fatigue. In dynamic testing the response to a load by the material is mostly time-dependent.

Fracture
A very simple description of fracture is: a separation, usually not wanted, in a solid under mechanical load at a temperature that is low compared to the melting temperature of that material. Fracture can be ductile as well as brittle. Fracture can result from tension, shear and compression. The description of fracture is most simple for tension. A ductile fracture under tension often shows the characteristic ‘cup-and-cone’ appearance.

A ductile fracture is preceded by substantial plastic deformation occurring in the region of fracture. Often, ductile fracture is accompanied by necking, as is the case for many metals and polymers during a tensile test. The less plastic the deformation the more brittle the fracture. A perfectly brittle fracture is defined as fracture without any plastic deformation. The material property characteristic for the material’s resistance against brittle crack growth is the fracture toughness (see Section 2.2.2). The same material can show both brittle and ductile fracture (see Figure 2.9), depending on shape and temperature.

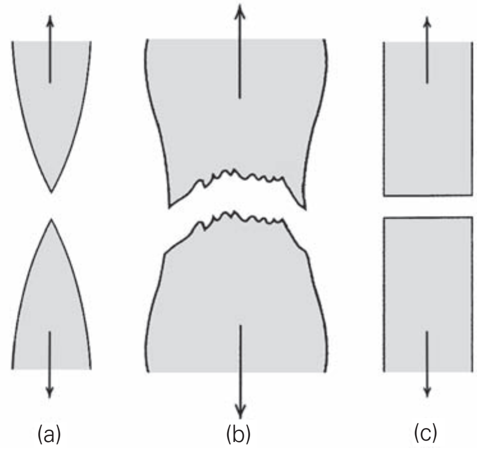


Figure 2.9. Morphology of fracture: (a) completely ductile; (b) ductile; (c) completely brittle.

Problem 2.11 *When fracture is inevitable, then a ductile fracture mode is preferable. Explain the reason why.*

The direction of brittle fracture is perpendicular to the direction of loading. The rate of brittle fracture is often very high and a brittle fracture surface is usually very smooth. Often this surface shows chevron-like lines. The chevron-lines may indicate the point of crack initiation. The tendency of a material to brittle fracture is important information for the designer and engineer. The fracture behaviour is determined by means of the Charpy impact test (see Figure 2.10) using a notched test specimen. This test is not an absolute method, it makes it possible to compare the fracture behaviour of different materials.

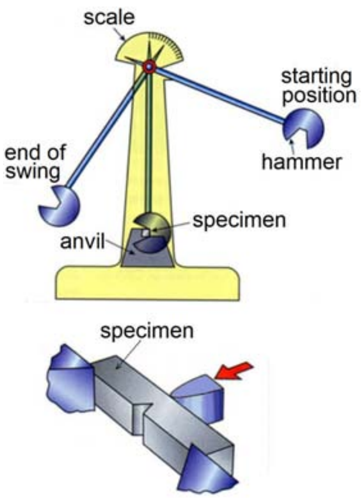


Figure 2.10. The Charpy impact test.

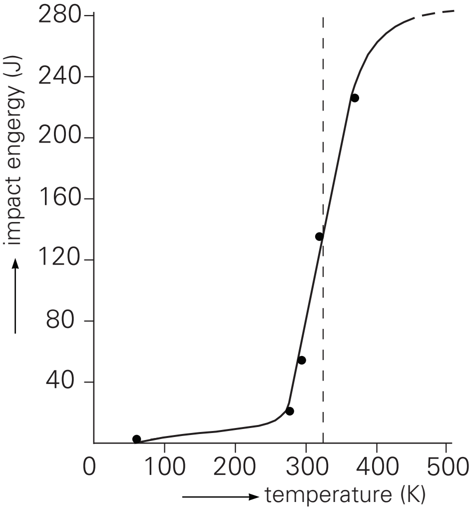


Figure 2.11. The impact energy for common mild steel as a function of temperature.

The energy lost by the swinging hammer per unit of cross-sectional fracture area is called the impact energy. This impact energy should not be confused with the fracture toughness. The impact energy can be plotted against the testing temperature. Many materials show a distinct temperature for the transition from ductile to brittle fracture (see Figure 2.11). This ductile-brittle transition is just below ambient temperature for many common mild steels and above 1000°C for many ceramics. Similarly, polymers often become brittle about 50°C below the so-called glass transition temperature at which the polymer structure changes into a more or less glassy state (see Section 3.5.3 for further details).

Creep

Creep is a continuous change of length under constant loading. Three elements are important in describing this process: stress, deformation and time. Intuitively it should be clear that an increase of temperature will cause an increase of the creep rate. To a certain extent, time and temperature are interchangeable in creep. Time is important, as the rate of the deformation characterizes the creep process (see Figure 2.12). Generally, the curve in between the two extreme curves in this Figure is considered as typical creep behaviour. The final stage of creep is fracture. In the first stage the creep rate decreases. The second stage is called secondary creep, which occurs at a constant creep rate. The third stage of creep is characterized by an increasing creep rate. In Stage II, for tensile creep, the creep rate can be written as:

$$\frac{d\varepsilon}{dt} = k\sigma^n \tag{2.26}$$

where k and n are material constants and σ is the applied stress.

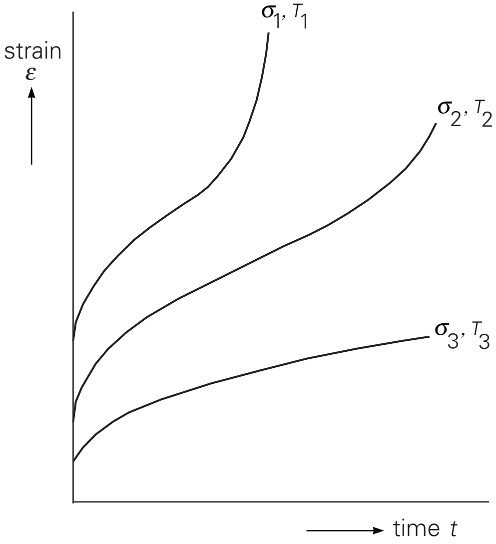


Figure 2.12. Creep (Anderson et al. (1991)).

For designers and engineers, the time to fracture at a certain stress level is important. Unfortunately it is impossible to measure this time to fracture for all possible stress cases. Extrapolation from the available experimental data is the only practical way out. For metals, the Larson-Miller parameter is often used (see Anderson *et al.* (1991)):

$$LM = 10^{-3}T(C + \log t_r) \tag{2.27}$$

With T = temperature in Kelvin, C = constant (mostly about 20) and t_r = time to fracture for creep (hours). The value of the LM parameter is a constant for a certain applied stress. The applied stress is shown as a function of the LM parameter in Figure 2.13.

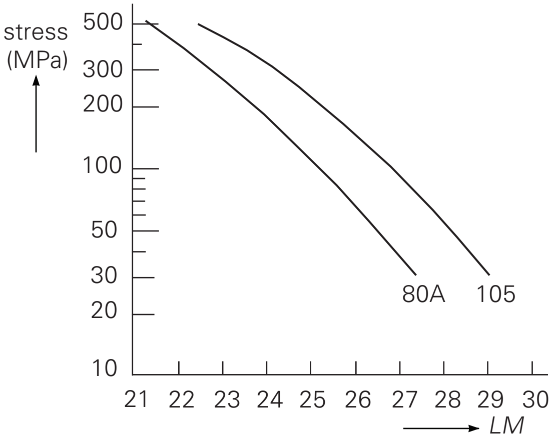


Figure 2.13. The applied stress as a function of the LM parameter for two Ni alloys (Anderson et al. (1991)).

Problem 2.12 *Determine the time to fracture for creep in case of the nickel alloy Nimonic 80A with an applied stress of 300 MPa at 800°C.*

The LM extrapolation clearly demonstrates the importance of the combination of applied stress or strain, the temperature and the type of material, see also Table 2.6.

Table 2.6. Overall conditions for creep.

material	*temperature*	*creep*
steel	< 300°C	unimportant
nickel alloys	> 500°C	important
aluminium alloys	> 100°C	important
polymers: thermoplastics	ambient	important

As mentioned before, three classes of polymers can be distinguished (see also Section 3.5): thermoplastics, thermosets and rubbers or elastomers. Creep is especially relevant for thermoplastics. Therefore, the *initial* E-modulus is not suitable to describe the long-term behaviour of thermoplastics under loading. Figure 2.14 schematically shows the creep of a polymer. The stress, σ, imposed at time $t = 0$, causes an immediate strain ε_0, which is related to the E-modulus *via* $\varepsilon_0 = \sigma/E_0$. Under continuous loading, ε increases over time. When at time t_1 the loading is removed, spontaneous relaxation occurs equal to ε_0, beyond that point the strain decreases gradually, sometimes becoming zero, or sometimes attaining a final value: the permanent plastic strain.

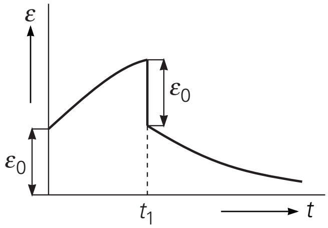


Figure 2.14. Schematic representation of creep.

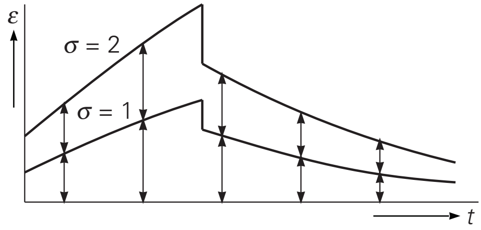


Figure 2.15. Linear viscoelastic behaviour.

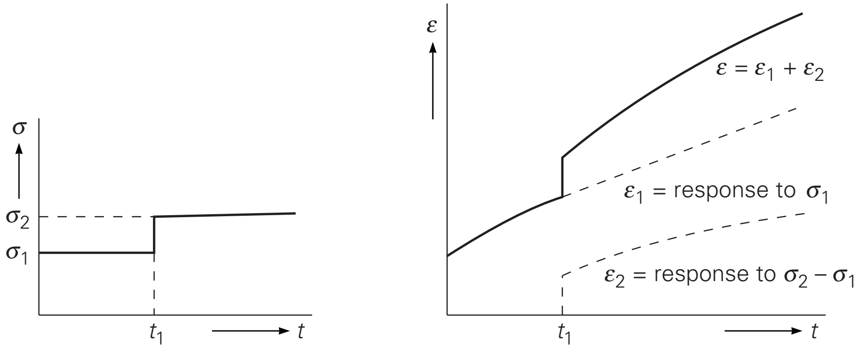


Figure 2.16. Superposition.

If the applied stress is doubled and if as a result the strain in the polymer specimen is doubled for every stress level, the polymer involved is called linear viscoelastic (see Figure 2.15). In such a case, the principle of superposition holds, as illustrated by Figure 2.16. Suppose a polymer is loaded by a stress σ_1 for a time t_1. The resulting strain is then $\varepsilon(t)$. At time t_1 the stress is increased abruptly from σ_1 to σ_2. Then for $t > t_1$, the strain of the polymer will contain two parts: the first part is the follow-up of the response to σ_1 *i.e.* $\varepsilon_1 = \varepsilon(\sigma_1, t)$. The second part is the response to the stress increase $\sigma_2 - \sigma_1$ with starting time $t = t_1$, *i.e.* $\varepsilon_2 = \varepsilon(\sigma_2 - \sigma_1, t - t_1)$. For $t > t_1$ the total deformation then becomes $\varepsilon = \varepsilon_1 + \varepsilon_2$. It goes without saying that the additional imposed stress may have an opposite sign, *i.e.* the stress is then decreased. This is illustrated by Figure 2.17. This superposition principle can be used to predict the form of the recovery curve after removal of the applied stress. For a continuously varying stress, superposition can be applied by approximating the varying stress by a sequence of small stepwise variations (see Figure 2.18).

To predict the behaviour of a polymer during deformation over long periods of time, creep data are essential. Creep data can be obtained from the open literature or may be provided by polymer suppliers. Creep data can be represented in various ways. The most simple method is to plot the strain ε as a function of time t at different stress levels, as shown by Figure 2.15. As time runs from seconds to years, time is always plotted on a logarithmic scale. Examples are shown in Figure 2.19.

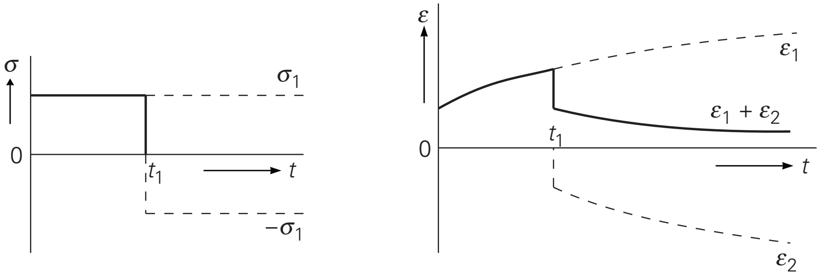


Figure 2.17. Shape recovery according to the superposition principle.

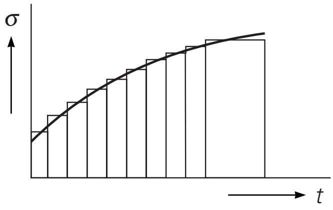
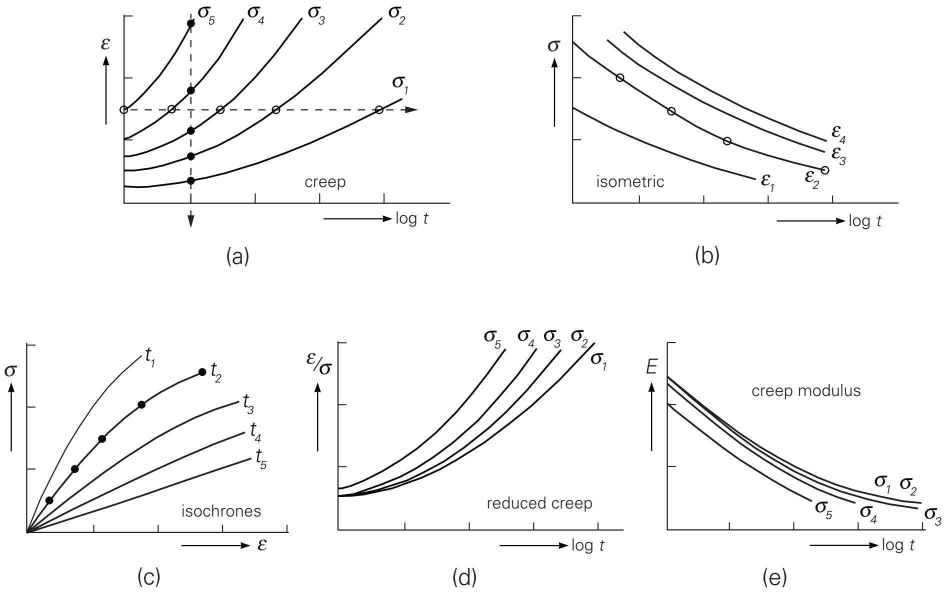


Figure 2.18. A stepwise approach of a continuously increasing stress.



(a)

(b)

(c)

(d)

(e)

Figure 2.19. Various representations of creep behaviour, $\sigma_5 > \sigma_4 > \sigma_3 > \sigma_2 > \sigma_1$.

From these creep curves two alternative representations can be derived. For a constant time t, the relation between stress and strain yields *isochrones* (Figure 2.19(*c*)), which should not to be confused with the σ-ε curves taken from a tensile test. At a constant value for the strain, *isometric creep curves* (Figure 2.19(*b*)) are obtained, which show the time needed to reach a certain strain at a certain stress level. Instead of the creep itself, the so-called *reduced creep* or *creep compliance* is often plotted as a function of time (see Figure 2.19(*d*)). Reduced creep is the strain divided by the stress, ε/σ. Deviations from linearity become visible as the curve involved deviates from the common curve, as is the case in Figure 2.19(*d*) for $\sigma = \sigma_3$ after a certain creep time. The ratio ε/σ has the dimension of a reciprocal modulus. The secant modulus σ/ε (see Equation (2.20)) is often denoted as the creep modulus. This creep modulus is given as a function of time by Figure 2.19(*e*).

Problem 2.13 *Demonstrate that in case of linear viscoelastic creep, the curves for the reduced creep at different stress levels coincide and that this also holds for the creep modulus curves.*

Isochrones are by far the most used representation of creep data. With their linear scales, isochrones are easy to read. The distance between isochrones is a measure for the creep rate, the curving is an indication for the deviation from linear viscoelastic behaviour. In most cases, it is possible to represent creep data for different temperatures with one band of isochrones. For each temperature, one axis can be depicted, see Figure 2.20. Creep is also often given in numerical terms like σ(1%,1000 h), *i.e.* the stress that yields a strain of 1% after 1000 hours of loading.

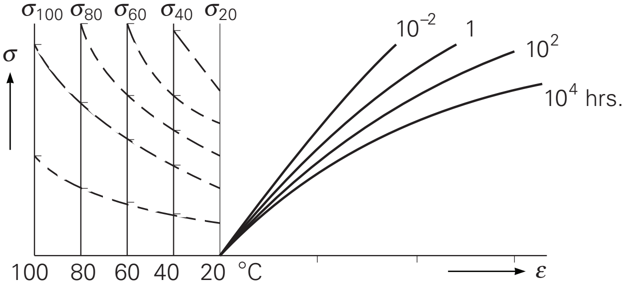


Figure 2.20. Isochrones for different temperatures (Van der Vegt (2006)).

A phenomenon closely linked to creep is *stress relaxation*. Stress relaxation is the ongoing continuous decrease of stress at a constant strain. The representation of stress relaxation may vary, examples are the stress σ as a function of log *t*, $E = \sigma/\varepsilon$ as a function of log *t*, or σ-ε isochrones. These relations do not correspond with the analogous ones for creep, but for practical conditions the differences occurring can be neglected. From the isochrones for creep stress relaxation can be derived, but only if the polymer behaviour does not deviate too much from linear viscoelasticity.

Fatigue

The overwhelming majority of undesired fractures occurs due to fatigue. Fatigue is caused by a varying or dynamic loading. In practice fatigue tests are performed by applying a dynamic load around a fixed average stress value, the mean stress σ_m. These variations of the applied stress are often more or less sinusoidal in time, see Figure 2.21(*a*) and (*b*). The stress amplitude is the stress variation around the fixed mean stress.

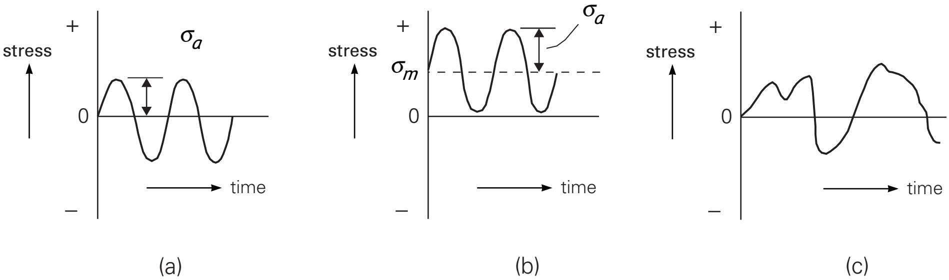


Figure 2.21. Stress cycles (Anderson et al. (1991)).

For a certain value of the mean stress, the magnitude of the cycle stress amplitude *S* causing fatigue fracture is measured as a function of the number *N* of loading cycles, yielding the *S*-*N* curves, also called the Wöhler curves (see Figure 2.22). It should be clear that for large values of *S* only a small number *N* of stress variations is needed to obtain fracture of the test specimen. Hence, the *S*-*N* curves roughly show a hyperbolic relation between *S* and *N*.

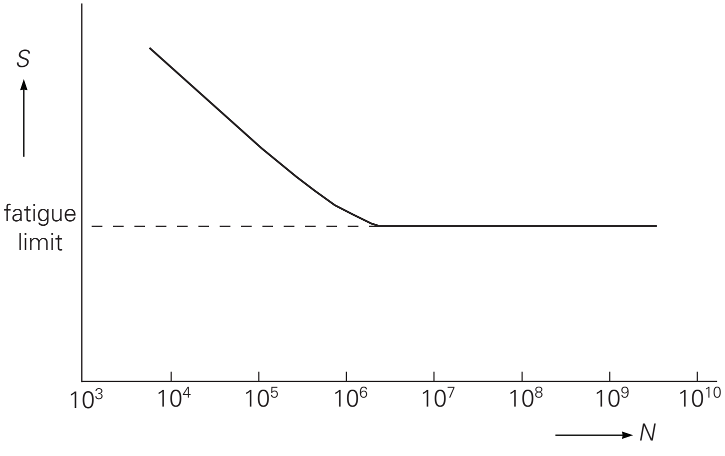


Figure 2.22. Schematic Wöhler curve for a plain carbon steel.

Some materials like steel and polypropylene show a stress amplitude for which an infinite number of stress variations yields *no fracture* at all. So, the *S-N* curve for steel can show a horizontal line (see Figure 2.22). The magnitude of the corresponding stress amplitude is called the fatigue limit for steel.

Most other materials show fatigue fracture at all numbers of loading cycles. This occurs at average stresses much lower than would be expected from the known values for σ_f or σ_y. The stress amplitude that causes fracture after a certain number of stress variations is often called the *fatigue strength* of that particular material.

The higher the mean stress applied, the smaller the stress amplitude yielding fracture or the shorter the lifetime of the specimen tested. If the mean stress is zero, the stress amplitude for fracture is maximal: σ_0. For other values of the mean stress σ_m, the safe upper limit of the stress amplitude can be estimated from:

$$\sigma_a = \sigma_0 \left(1 - \frac{\sigma_m}{\sigma_y} \right) \tag{2.28}$$

In order to estimate the lifetime of a construction under stress variations Miner's Rule can be used. Suppose, during one month of application the following stress variations occur in a part of a construction: n_1 variations with amplitude σ_1, n_2 with amplitude σ_2, n_3 with amplitude σ_3 and, generally, n_i with amplitude σ_i. Suppose further that N_1, N_2, N_3 and N_i are the number of variations corresponding to failure for the various stress amplitudes. It is clear that a construction can show failure only once. Each of the combinations of stress amplitude and number of cycles represents a fraction n/N of the total lifetime. Miner's Rule states that failure occurs when:

$$\sum_i \frac{n_i}{N_i} = 1 \tag{2.29}$$

Miner's Rule is not very accurate and can only be used as a first estimate for the lifetime of a construction. The following example is an application of Miner's Rule (Weidman *et al*. (1994)).

A construction part made of the aluminium alloy 2014-T6 was loaded for one month according to the following data:

number of stress variations	*stress amplitude involved*
20	210 MPa
400	140 MPa
1000	70 MPa

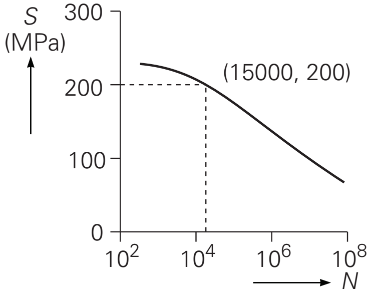


Figure 2.23. Stress amplitude as function of the number of loading cycles for the aluminium alloy 2014-T6. The mean stress equals the stress amplitude.

The *S-N* curve for the aluminium alloy involved is given in Figure 2.23. The estimation for the lifetime using Miner's Rule runs as follows. First Figure 2.23 gives the number of stress cycles at which the given stress amplitudes would be fatal:

$$200\ \text{MPa} \rightarrow 10^4 \qquad 140\ \text{MPa} \rightarrow 10^6 \qquad 70\ \text{MPa} \rightarrow 10^8$$

Application of Miner's Rule then yields:

$$20/10^4 + 400/10^6 + 1000/10^8 = 24{\cdot}10^{-4}$$

So the estimated lifetime of the construction part is: $(24{\cdot}10^{-4})^{-1}$ months = 35 years.

2.4 Electrochemical corrosion of metals

Products have interactions with their environment during their application. These interactions are often damaging. Metals rust or corrode, polymers can age (see Section 7.4) and ceramics can react with gases from their environment. This section is limited to electrochemical corrosion of metals and their alloys, which is mostly equivalent to corrosion of metals and alloys in an aqueous environment. In contact with water, a metal always shows the tendency to dissolve; *i.e.* an atom detaches itself from the metal, leaves a number of electrons behind and is transferred as a positive ion into the aqueous solution. In its turn, the piece of metal in water contact gains a surplus of a negative charge. This transferring reaction is called *oxidation* and is represented by:

$$Me \rightarrow Me^{n+} + n\ e \tag{2.30}$$

In absence of an external electricity source, a site elsewhere on the same piece of metal having a contra-reaction maintains charge neutrality. This contra-reaction is called *reduction*. In case the solution contains hydrogen ions, the following reaction can proceed as reduction:

$$2\ H^+ + 2\ e \rightarrow H_2 \tag{2.31}$$

In case the solution contains dissolved oxygen:

$$O_2 + 4\ H^+ + 4\ e \rightarrow 2\ H_2O \tag{2.32}$$

Reaction (2.30) supplies just the number of electrons to be consumed during reactions (2.31) and/or (2.32). Hence, the electrical neutrality is maintained, while the metal is effectively dissolved. In daily life this process is called *corrosion*. The aqueous solutions now contain ions. Such a liquid is commonly referred to as an electrolytic solution. The site of the metal at which the oxidation occurs is called the *anode*. The corresponding site with the reduction is called the *cathode*. To maintain electroneutrality a flow of electrons is necessary. Apparently, there exists a potential difference between anodic and cathodic sites.

As said before, a metal placed in an aqueous solution possesses the tendency to send positively charged ions into that solution. This tendency is called the electrochemical potential with regard to the solution. That tendency is different for different metals, when placed into the same solution. Suppose, two different metals are placed into the same solution. Then, there is a difference in potential between those two metals. This difference can be measured as an electrical tension between the two metals. The two metals placed into the solution form together an electrochemical cell consisting of two half-cells, with each a metal placed into the solution. A half-cell with a pure metal placed into an aqueous solution of 1 M of its ions at 298 K and 1 atm is called the standard half-cell (1 M = 1 mol/litre). Suppose that the concentration of the ions in the standard half-cell is constant under the given conditions. By definition, the standard half-cell with 1 M hydrogen ions and bubbling hydrogen gas against platinum has a zero potential. Along the platinum, reduction reaction (2.31) proceeds. As only differences in potential can be measured, the potentials of the different half-cells are measured and given with respect to the standard hydrogen cell with bubbling hydrogen gas. The values of all those potential differences with respect to the standard hydrogen half-cell can be arranged in decreasing order. The result is commonly known as the standard electrochemical series (see Table 2.7). At the top of the series, there are the inert metals and the reactive metals are at the bottom of the series (with the half-cell reactions represented as reductions).

Table 2.7. Electrochemical series.

half-cell reaction			*standard electrode potential in volts*
$Au^{3+} + 3\ e$	→	Au	1.420
$O_2 + 4\ H^+$	→	$2\ H_2O$	1.229
$Pt^{2+} + 2\ e$	→	Pt	1.200
$Ag^+ + e$	→	Ag	0.800
$Fe^{3+} + 3\ e$	→	Fe	0.771
$O_2 + 2\ H_2O + 4\ e$	→	$4\ OH^-$	0.401
$Cu^{2+} + 2\ e$	→	Cu	0.340
$2\ H^+ + 2\ e$	→	H_2	0.000
$Pb^{2+} + 2\ e$	→	Pb	– 0.126
$Sn^{2+} + 2\ e$	→	Sn	– 0.136
$Ni^{2+} + 2\ e$	→	Ni	– 0.250
$Co^{2+} + 2\ e$	→	Co	– 0.277
$Cd^{2+} + 2\ e$	→	Cd	– 0.403
$Fe^{2+} + 2\ e$	→	Fe	– 0.440
$Cr^{3+} + 3\ e$	→	Cr	– 0.744
$Zn^{2+} + 2\ e$	→	Zn	– 0.763
$Al^{3+} + 3\ e$	→	Al	– 1.662
$Mg^{2+} + 2\ e$	→	Mg	– 2.363
$Na^+ + e$	→	Na	– 2.714
$K^+ + e$	→	K	– 2.924

Consider two metals, Me_1 en Me_2. Both metals are in contact with an electrolytic solution with an ion concentration of 1 M, for both the corresponding ions. Outside the solution, the metals make a conducting contact. For the potential difference can be written:

$$\begin{array}{lcll} Me_1 & \rightarrow & Me_1^{n+} + n\ e & -V_1 \qquad \textit{oxidation} \\ Me_2^{n+} + n\ e & \rightarrow & Me_2 & +V_2 \qquad \textit{reduction} \\ \hline Me_2^{n+} + Me_1 & \rightarrow & Me_2 + Me_1^{n+} & \Delta V = V_2 - V_1 \end{array}$$

Here V_1 and V_2 are the standard potentials taken from the electrochemical series, respectively. If $\Delta V > 0$, then the reaction proceeds in the direction indicated. If $\Delta V < 0$, then the reaction has the opposite direction. Hence, the electrochemical series can be applied to predict which metal will replace another metal from an electrolytic solution.

The above defined standard half-cells do not exist, of course, in more practical situations. Therefore, the reactions of Table 2.7 are often arranged according to potential differences as measured against other half-cells with other aqueous electrolyte solutions. These arrangements are called the standard galvanic series.

Problem 2.14 *Do you expect that the sequence of the reduction reactions in the galvanic series differs from that in the electrochemical series? Give a reason for your expectation.*

Metal constructions and metal products are often in aqueous contact during their application. In the overwhelming majority of cases, the temperature of application is room temperature, *i.e.* in the vicinity of the temperature of the standard electrochemical series. The classic example of such a case is a Dutch bike in a rain shower. The foregoing text directly leads to three conditions necessary for electrochemical corrosion of a metal:

1. the possibility of an anodic reaction,
2. the possibility of a cathodic reaction,
3. the possibility of an electric contact between anodic and cathodic sites.

Problem 2.15 *Describe four fundamental approaches to prevention of electrochemical corrosion by the designer.*

2.5 The value of material properties

As said before, the fundamental properties of materials are directly related to the physical structure of matter and materials. For these properties, the accuracy of data depends mainly on the available measuring apparatus. The elastic constants are examples of this class of properties, as will be made clear with an example in the next chapter. However, the values of the majority of materials properties, of course including the ‘abilities’ (see Section 2.1), also depend on preparation and measuring procedures. Hence, standardization of preparation and procedures is essential to maximize the validity of the comparisons made on the basis of the values for material properties. This is especially true for the processing properties encountered in the transitions from matter into materials. The methodological ideal that a measurement does not affect the outcome is unattainable. Furthermore, stochastic variations inevitably occur during specimen preparation. Despite the ongoing standardization of testing conditions, each value of a material property is a stochastic or a statistical number. *The* yield strength of a material does not exist. The decisive question for a designer or an engineer is not the value of this or that material property, but the probability of failure occurring in a specific product made out of a specific material. To find an answer to this question the entire production process has to be considered.

Chapter 3

Structure of materials

3.1 Introduction

Materials can be studied from a phenomenological point of view: which materials are found in modern society, which resources are used to make them and which features are important for their applications in real products? In many cases, the mechanical properties (how strong is a material?) are decisive. However, other properties may play a role, for instance surface and corrosion characteristics can determine the success or failure of a product. The strength of steel is usually higher than that of aluminium alloys, but steel often shows severe corrosion compared to aluminium alloys. Or, as another example, the density of polymers is lower than that of most metals, which can be an important factor in designing lightweight constructions.

This chapter will provide further insight into the structure of materials. With the word structure we mean the way the atoms or molecules are assembled to form the substances commonly known as materials. This insight may help to explain the relation between properties and the processing route by which products are manufactured. It is important to understand that a material is a substance processed into a real final product or a semi-finished product. Material properties and characteristics should be considered together with the intended product and its manufacturing route. Product (design), Material and Manufacture are closely related *via* the **PMM** triangle (see Figure 3.1).

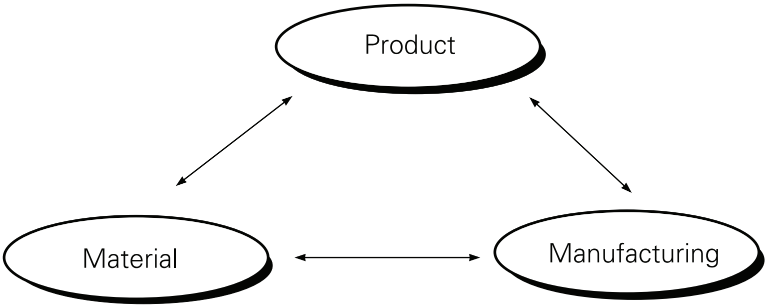


Figure 3.1. The triangle Product, Material and Manufacturing.

The influences exerted during processing have an effect on the material properties of the final product. Hence it can be said that materials science is in a way a 'historical' science. Some examples may serve as an illustration:

1. Many aluminium alloys can readily be deformed at ambient temperatures. If this deformation is performed below the recovery temperature (see Section 3.3.3), it is called cold deformation, which results in increased hardness. The hardness of a product produced via cold deformation then depends on the manufacturing route. The extent to which aluminium alloys can undergo a cold deformation, depends on i. the crystal lattice (see Section 3.3), ii. the grain size (see Section 3.3) and iii. the presence or absence of precipitates (see Section 6.2). These three aspects together determine the structure of the aluminium alloy.
2. A common pair of scissors is made of an iron-carbon alloy. By definition, steel is an iron-carbon alloy with less than 2 wt% carbon (see Section 5.3). Steel for such a pair of scissors contains so much carbon that cold deformation is impossible. Therefore, the manufacturing proceeds *via* (hot) forging. Afterwards, the steel is hardened. The structure of the material selected for the pair of scissors determines the properties of the final product, as well as the manufacturing route.
3. Plastic cups are often produced from polystyrene (see Section 7.1). Plastics are macromolecular substances containing large chain molecules. Such materials are fully transparent if the polymer chains are randomly distributed. This is the case in a transparent polystyrene cup. Polystyrene foams are often used for packaging. These foams contain about 90 vol% air, the rest consists of polystyrene walls. Foams are opaque, so it can be concluded that the properties, in this case the optical properties, of the material are strongly related with the structure of the final product.

The above examples clearly show the importance of structure for the properties of materials and of the final product. The appearance of the product (*e.g.* surface finishing and colour) may also be determined by the material properties and hence by the material structure. As interactions exist between structure, processing technologies and materials selection, even the dimensions and shape of a product can be linked to structure and properties, *e.g.* a welded product has a different appearance than a cast product made from the same material. Hence, it is obvious that materials selection and processing technologies have major implications on the design as well as on the product performance. The second and third examples demonstrate the strong link between composition and structure.

In practice, materials are mostly mixtures of different substances. Metals are mostly alloys and polymers are often blends or composites. We will discuss the relation between chemical composition and structure using some applied thermodynamics in Chapter 4. It will be shown that the structure of materials can depend on temperature. For example, iron above 912°C shows a different structure to that at room temperature (see Chapter 5). Hence, heat treatment can influence structure and can change the properties of a material (Chapters 5 and 6).

3.2 Atoms and atomic bonds

All matter consists of atoms. Nature has about 90 different atomic species forming the elements. To first approximation, atoms are spherical and have a diameter of about 0.3 nm (1 nm = 10^{-9} m). Atoms have an electrically positive nucleus surrounded by a cloud of electrically negative particles called electrons. The nucleus consists of protons and neutrons, the protons give the nucleus its positive charge and the neutrons are electrically neutral. Also, the atom as a whole is electrically neutral, the number of protons equals that of the electrons. Each element has an atom number equal to the number of protons in the nucleus. The mass of an atom is mainly determined by the sum of the numbers of protons and neutrons, as the mass of the electrons is negligible. Atoms with the same number of protons but with different numbers of neutrons are called isotopes. Isotopes have identical chemical properties, but may differ with respect to their physical properties.

The cloud of electrons occupies different shells around the nucleus. These shells do not have sharp boundaries, but the electron density differs from shell to shell. The shell number (symbol n) takes values of n = 1, 2, 3, 4, 5, 6, 7, 8 …., where increasing numbers indicate larger distances from the nucleus. The structure of these shells, especially that of the outermost shell, to a large extent determines the physical and chemical properties of the atoms. For example, the chemical bonding properties of atoms, which in turn are responsible for the mechanical properties of materials, are governed by the outermost shell(s).

The structures of the electron shells of the different elements show certain regularities. These form the basis of the so-called Periodic Table of the Elements (see inside cover). Starting from the nucleus, the first shell is occupied with at most 2 electrons, the second with at most 8, the third with at most 18, the fourth shell with at most 32, and in general the shell with number n contains at most $2n^2$ electrons. However, the outer shell never contains more than 8 electrons. The electrons in the outer shell are called the valence electrons. The number of valence electrons largely determines the chemical properties of the element involved. The outer shell is not necessarily completely filled up. The elements with full outer shells are chemically inactive (see Table 3.1), they form the group of the inert gases. It appears that on establishing chemical bonds, all atom species strive for this so-called inert gas configuration. This is possible by either taking up or losing some valence electrons. An element behaves like a metal when it loses valence electrons, whereas a non-metal takes up valence electrons.

Table 3.1. Inert gas configuration.

number of shells	*number of electrons*	*inert gas*
n = 1	2	helium
n = 2	2 + 8	neon
n = 3	2 + 8 + 8	argon
n = 4	2 + 8 + 18 + 8	krypton
n = 5	2 + 8 + 18 + 18 + 8	xenon
n = 6	2 + 8 + 18 + 32 + 18 +8	radon

Elements with the same number of valence electrons, but different number of electrons in the inner shells have similar chemical properties. Examples are the alkali metals Li, Na, K, Rb, Cs, Fr, and the halogens F, Cl, Br, I, At, respectively, with one and seven electrons in the outermost shell. The Periodic Table of the Elements arranges the elements according to increasing atom number in rows with a common number of shells where the elements with the same number of valence atoms are placed in columns. The metals that can easily lose their valence electrons, are situated in the left part of the Periodic Table, whereas the non-metals are situated in the right part of the Table. From left to right, the metal features are gradually replaced by non-metal characteristics.

The tendency of atoms to form the inert gas configuration governs the formation of chemical bonds. The type of chemical bond depends on the number of valence electrons involved. For instance, overlapping of electron shells of corresponding or different elements can result in an inert gas configuration and this causes a bond between these atoms to be formed. Such a combination of two or more atoms is called a molecule. There are three main types of bonding, where it should be remarked that this distinction is not very sharp. In practice, mixed forms of bonding occur. The following types of bonding are distinguished: ionic or heteropolar bonding, covalent or homopolar bonding and metal bonding. All these types of bonding involve structural changes of the outer shells and are called the primary bonds. Besides, there are bonds without changes of the structure of the outer shell. Those bonds are called secondary bonds, examples are Van der Waals bonds and hydrogen bonds.

Ionic or heteropolar bonding

Ionic bonding results from the attraction forces between ions with charges of opposite signs. Ions are formed when metal atoms lose one or more of their valence electrons (metal ions are thus positive) or when non-metal atoms take up valence electrons (hence non-metal ions are negative). Due to the electrostatic attraction a bond is established between ions of different signs (see Figure 3.2). This bonding is called the ionic bonding. In solids based on ionic bonds, crystallization takes place resulting in a very regular arrangement of the ions. This regular arrangement stems from the fact that a negative ion attracts each positive charge and *vice versa*. The distance between the ions is determined by the magnitude of the electrostatic attracting forces involved. A well-known example of ionic bonding is given by rock salt, NaCl (see Figure 3.3).

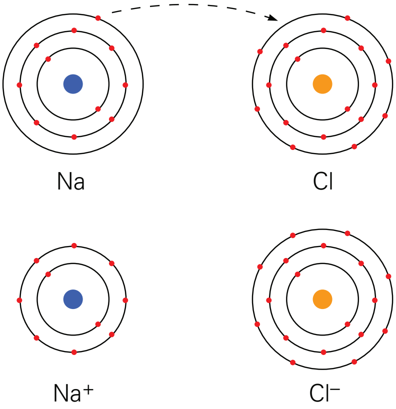


Figure 3.2. Ionic bonding in NaCl.

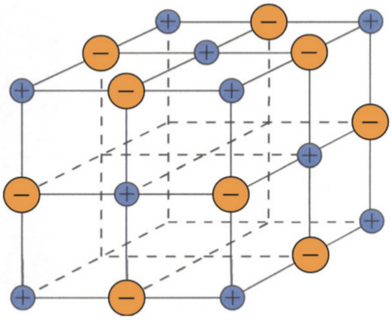


Figure 3.3. The ionic lattice of NaCl ($+ = Na^+$, $- = Cl^-$).

Covalent or homopolar bonding

The covalent bond especially occurs with the non-metals, such as oxygen, O_2 or chlorine, Cl_2. The inert gas configuration is obtained by the sharing of one or more valence electrons by both atoms (see Figure 3.4).

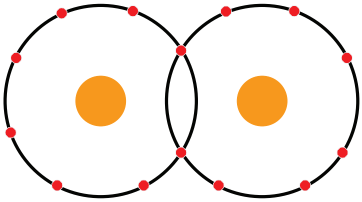


Figure 3.4. A diatomic molecule with covalent bonding.

Covalent bonds can also occur with different atoms. This type of bonding is especially important for organic compounds. The carbon atom has four valence electrons in elliptic trajectories with their long axis directed to the corners of a tetrahedron. In each of these directions, another electron can form a covalent bond. Methane, CH_4, serves as an example (see Figure 3.5). The mutual bond of the carbon atoms in chain molecules (see Section 3.5) is covalent too. Carbon atoms can also form double bonds, like in ethylene ($CH_2{=}CH_2$). Such double bonds play a role in the formation of long chain molecules (polymerization), which is important for the plastics industry.

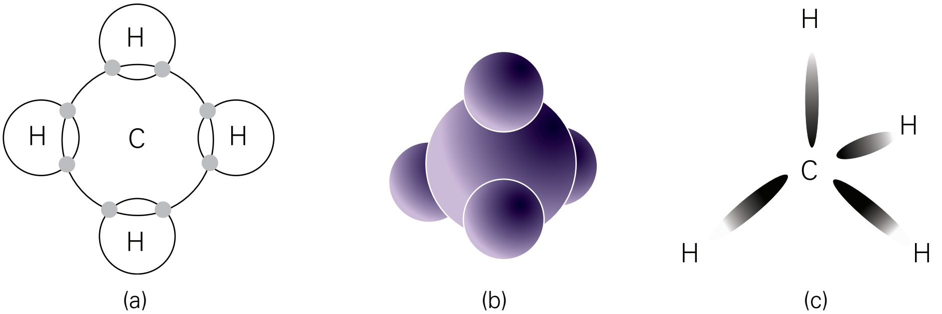


Figure 3.5. CH_4 (methane) models: (a) a two-dimensional model; (b) a three-dimensional model; (c) the model for the covalent electrons.

Metal bonding

In a metal, the valence electrons are not confined to specific atoms, but are shared by all atoms present in the solid. A metallic crystal consists of a regular ordering of positive ions where the valence electrons are able to move around freely (see Figure 3.6).

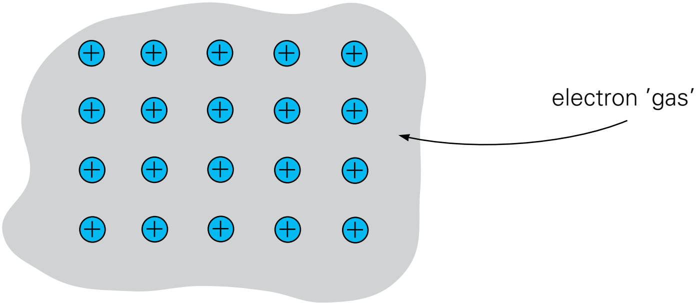
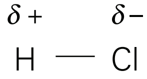


Figure 3.6. Metal bonding.

Nevertheless, in common speech these positive ions are often called metal atoms. The valence electrons are not localized with respect to a specific ion. However, the other electron shells of the metal ions remain localized. The collective freely moving valence electrons in the metal are called the ‘electron gas’. This electron gas is responsible for the binding of the metal ions. As a rule metal bonding is slightly weaker than covalent and ionic bonding.

Transitions between covalent and ionic bonding: dipole formation and secondary bonding

In a non-metal molecule with two equal atoms like Cl_2, the valence electrons are evenly distributed between the two atoms. The molecule is electrically symmetric. However, in many molecules the electrons are partially transferred from one atom to another. These molecules have bonds that can be considered as combinations of covalent and ionic bonding. The molecule of hydrochloric acid gas (HCl) can serve as an example. The common valence electron is much more localized in the vicinity of the Cl atom than in the neighbourhood of the H atom, resulting in a certain *polarity* of the molecule. This is illustrated by Figure 3.7, where the symbol δ represents a partial electric charge; it does not reflect the displacement of a full elementary charge as in the case of ions. This can be summarized by: ‘a molecule with polarity has a permanent electric dipole’.



$$\overset{\delta+}{\mathrm{H}} — \overset{\delta-}{\mathrm{Cl}}$$

Figure 3.7. The polar HCl molecule, a permanent dipole.

Permanent electric dipoles can be present in a molecule, as we have seen in the case of HCl. However, also non-polar molecules may show weak dipole behaviour. As electrons follow paths around the nucleus, the midpoints of the negative and positive charges in an atom will not constantly coincide. Hence, an atom can be considered as a weak fluctuating dipole with a constantly changing direction. A neighbouring atom will feel the influence of the fluctuating dipole in the first atom: in the second atom a dipole is induced. Van der Waals or secondary bonding is based on the attraction forces between these fluctuating dipoles. The number of atoms or molecules involved in these secondary bonds is not specified. Secondary bonding is much weaker than primary bonding. While the primary bonding governs the chemical structure of molecules, the Van der Waals bonding is related to the intermolecular forces that govern the physical properties of molecular compounds. A special example can be found in the case of water molecules (see Figure 3.8). Here, this type of interaction, a hydrogen bond, results in a high boiling point and a large heat of evaporation compared to compounds of comparable molecular mass.

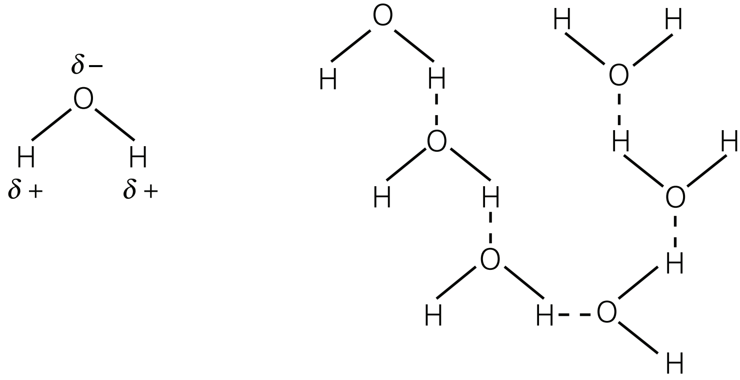


Figure 3.8. The polar water molecule and the hydrogen bonding in liquid water.

The hydrogen bond, or hydrogen bridge, is a special interaction mainly involving hydrogen and oxygen, like in water, or hydrogen and nitrogen. In many polymers the secondary bonding not only determines the physical characteristics (like the melting point), but also the mechanical properties. As a matter of fact, the covalent bonds of the polymer chain molecules are only rarely directly loaded. From the above short discussion on bonding, one striking conclusion emerges: polymers in general will show much less strength and stiffness than metals (metal bonding) and ceramics (ionic binding) which are held together by primary bonds.

3.3 Metal crystals

3.3.1 Lattices

Many solids are crystalline. This indicates that these solids show a nearly perfect arrangement of atoms. The atoms are regularly arranged forming well-defined planes. These planes can be seen in the regular shape of rock salt (NaCl) and other crystals. Ordering of atoms and/or molecules has a great impact on the properties of solids. The covalent bonds between carbon atoms can result in a very rigid and strong structure as in diamond. A mixed ion/covalent bonding occurs in a very important class of materials based on silicon dioxide (SiO_2). Silicon dioxide can form either an ordered crystalline structure (quartz) as well as a rather unordered one (glass). Quartz is characterized by the fact that the silicon and oxygen atoms occupy fixed positions in a space-filling network, while in glass the SiO_2 molecules are arranged randomly. The structure of glass is generally described as being amorphous (*literally*: ‘without shape’).

Glass and diamond are extremes. Metals hold a position in-between. Metal atoms are ordered in a crystal structure. However, a piece of metal consists of a large number of crystals each with a different orientation. Such crystalline regions are called grains or crystallites. The grain size of a metal is important for its properties. At a grain boundary the orientation of the crystal structure abruptly changes. The grain boundary is the section of the interface between two grains, and as such is disordered.

Typical interatomic distances in metals are about 0.3 nm. Atoms perform vibrations (at ambient temperature with a frequency of about 10^{13} Hz). On heating the amplitude of the vibrations increases, the metal expands. The atomic vibrations hinder the movement of the free electrons, which means that in general the electric resistance increases with temperature.

For most metals, their crystal structure is surprisingly simple. The smallest unit that defines the entire three-dimensional crystal structure is called the unit cell. Stacking the unit cells to form a space-filling structure generates the crystal system. Several crystal systems are important for metals:

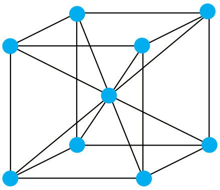
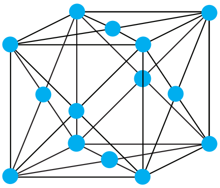
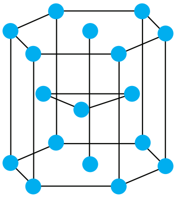
1. Cubic:	the unit cell is a cube: three mutually perpendicular axes of equal length.
2. Tetragonal:	the unit cell is a rectangular block: three mutually perpendicular axes of two different lengths.
3. Hexagonal:	the unit cell is a hexagonal prism: three axes of equal lengths with inner corners of 120° and the fourth axis of different length perpendicular to the plane through the other axes.

Atoms can occupy the unit cells in different ways. The geometry of this occupation is called the crystal lattice. The lengths of the axes are characteristic for the size of the cell and are called the lattice parameters or lattice constants. For the cubic lattice the lattice parameter equals the edge of the cubic cell. For metals the following lattices are important (see Table 3.2):

a. body-centred cubic (BCC),
b. face-centred cubic (FCC),
c. hexagonal close-packed (HCP).

The metal bonding is caused by the valence electrons giving equal binding forces in all directions. These forces are so strong that the metal ions are brought together as close as possible. So, preferably, a close-packed ordering of the metal ions occurs: each ion has a maximum number of twelve neighbours. The FCC and HCP lattices are indeed close-packed. In these cases the atomic packing factor, *i.e.* the volume fraction of the spherical atoms in the unit cell, is 0.74. Sometimes the binding forces are a little less effective and a somewhat more spacious packing develops: the BCC lattice where each atom has only eight neighbours. Consequently, the atomic packing factor is also lower: 0.68. The second column of Table 3.2 gives the schematic representation of the BCC, FCC and HCP lattices. The small spheres represent the approximate midpoint positions of the atoms. In reality, all metal ions touch each other in the close-packed HCP and FCC lattices, while in the BCC lattice this only occurs on the cube body diagonal. The BCC crystal is shown in Table 3.2 and Figure 3.9.

Table 3.2. Crystal lattices for metals.

lattice	*illustration*	*examples*
BCC		W, Mo, α-Fe
FCC		Cu, Al, Au, Ni, Pb, γ-Fe
HCP		Mg, Zn, Ti

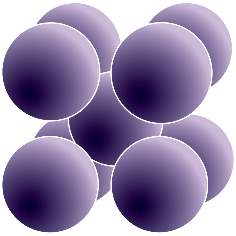


Figure 3.9. Atoms on a body-centered cubic lattice (BCC).

Problem 3.1 *For the BCC lattice, the cube diagonals are the most densely packed directions. Verify that the BCC lattice provides each atom with only eight nearest neighbours.*

A closest-packed layer is shown in Figure 3.10. A better occupation of the available space is not possible. In the layer, each atom has six neighbours. Between the atoms, seen from above, open triangles can be discerned: those with the vertices up in Figure 3.10 are arbitrarily designated as B positions and those with the vertex down by C.

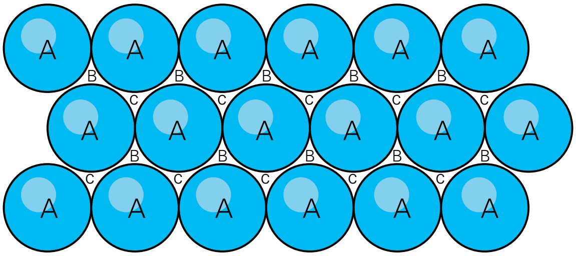
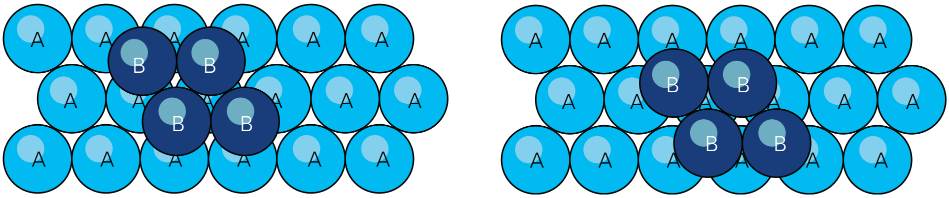


Figure 3.10. A close-packed layer.

When a second close-packed layer is put on the first, it may be positioned with the centres of its atoms over either the B or the C sites. At this point both are equivalent as can be concluded from Figure 3.11 or by rotating Figure 3.10 by 180°.



stacking of the second layer on the B positions of the first layer

stacking of the second layer on the C positions of the first layer

Figure 3.11. Stacking on the B sites is identical with stacking on the C sites.

For the third layer we are faced with a choice, as can be concluded from Figure 3.12. The atoms may be aligned directly above the A atoms of the first layer (see Figure 3.12(*a*)). This stacking is repeated over and over and leads to the sequence ABABAB…, every other layer is the same. The result is the HCP crystal lattice as illustrated in Table 3.2 and Figure 3.13. The other option is that the centres of the atoms of the third layer (C atoms), nesting in the B or C sites of the second layer, are positioned above, respectively, the C or B sites of the first layer, as shown in Figure 3.12(*b*). This yields an ABCABC… stacking sequence, the layers are repeated every third plane. The resulting crystal lattice is FCC (see Figure 3.14).

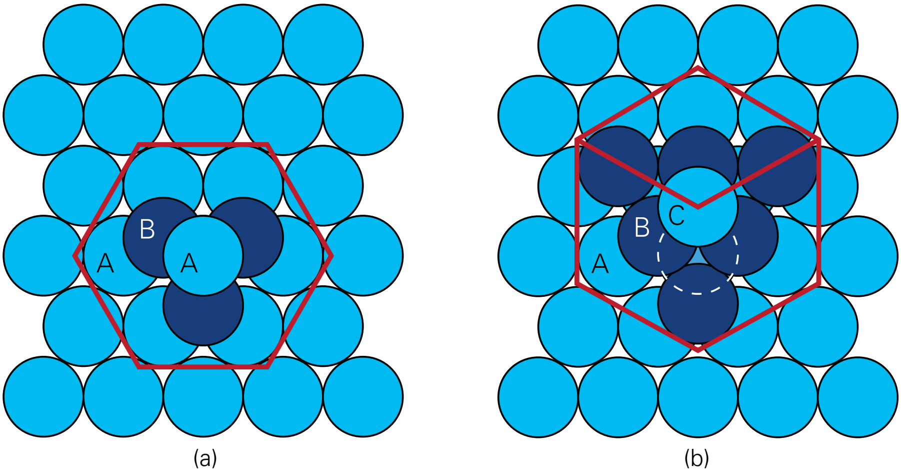


Figure 3.12. Stacking of the third layer of atoms: (a) HCP; (b) FCC.

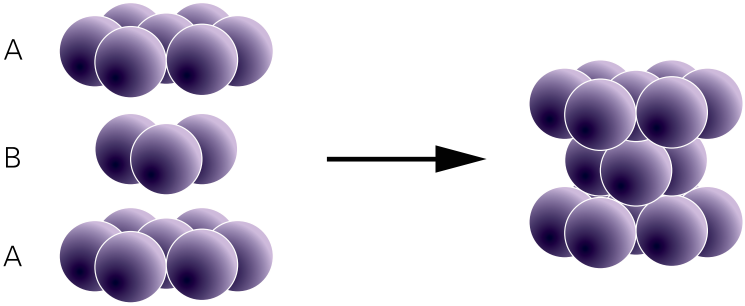


Figure 3.13. Hexagonal close-packed crystal (HCP).

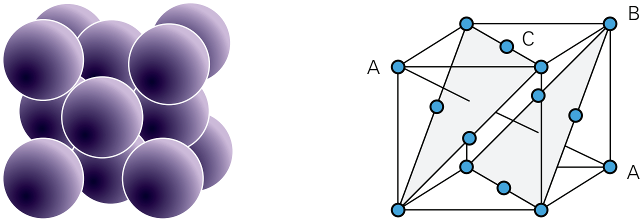


Figure 3.14. Face-centered cubic crystal (FCC).

Apart from the stacking sequence both close-packed lattices are very much alike. The FCC stacking may easily be converted to the HCP stacking by a translation of the uppermost sphere, as shown by the dashed white outline in Figure 3.12(*b*).

Problem 3.2 *Verify that the cube diagonal of the FCC lattice is an axis of three-fold symmetry.*

When the atoms are considered to be hard spheres, the atomic packing factor (APF) is less than one for all lattices, its maximal value is 0.74 for the close-packed lattices HCP and FCC, as mentioned before. Hence, in each lattice free spaces or cavities are present. In close-packed lattices tetrahedral and octahedral cavities are found (see Figure 3.15). The BCC lattice shows cavities on the midpoints of the cube axes and on the cube planes. For this lattice, each cavity is surrounded by six atoms, two nearby and four further away. These six atoms form an irregular octahedron (see Figure 3.16). The connecting line of the two nearby atoms is the octahedron axis. The cavities on these lines parallel to the X, Y and Z axes are accordingly denoted as X, Y and Z type cavities. Every atom is surrounded by one cavity of each type. Thus the total number of cavities is three times the number of atoms.

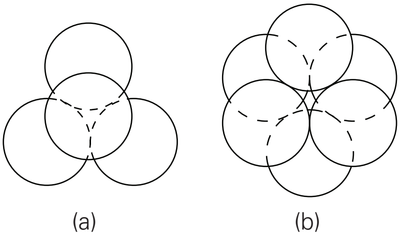


Figure 3.15. (a) Tetrahedral cavities; (b) octahedral cavities.

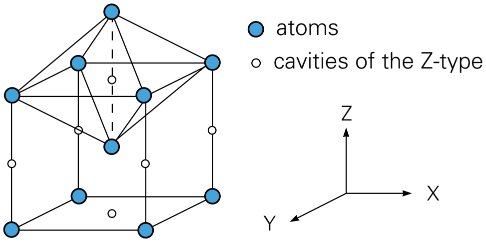


Figure 3.16. Irregular octahedron with Z type cavities.

Problem 3.3 *Show that the cavities for BCC are all identical.*

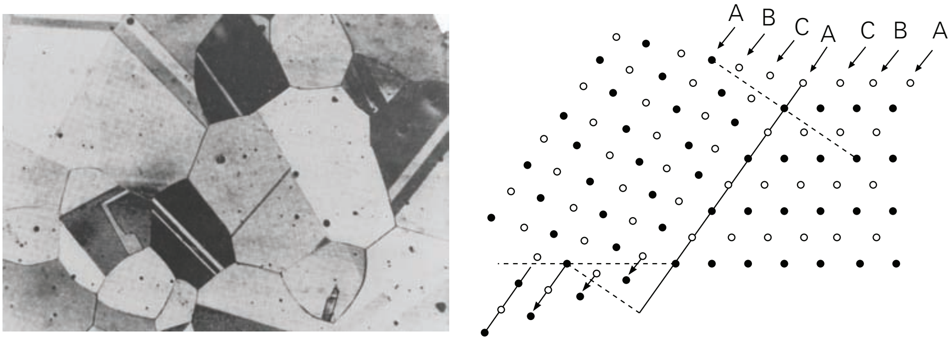


Figure 3.17. Recrystallization twins in copper (note that the positions have mirror symmetry with regard to the full line).

A metal crystal can be regarded as a part of space where the lattice has a certain specific orientation. Usually, the orientations of the lattices in neighbouring metal crystals are unrelated. However, occasionally it may happen that the lattices of neighbouring grains are such that the metal atom positions form a mirror image on both sides of the grain boundary. Such crystal structures are called twinned crystals, or in short twins. The interface between those twins is commonly called the twin plane. Twins can arise on deformation and recrystallization (see later in this chapter). Twins resulting from recrystallization often occur in copper alloys (see Figure 3.17).

3.3.2 Imperfections in crystals

Real metal crystals are imperfect compared to the lattices discussed above. These imperfections have a large impact on many properties, like mechanical strength, deformation and surface characteristics. Three different types of imperfections can be discerned: point, linear and plane defects.

Point defects

A frequently occurring point imperfection is the unoccupied atomic position, a vacancy. These vacancies are the result of the thermal motion of the metal ions. The ions vibrate around fixed positions, but there is a small chance that an ion with sufficient energy leaves its equilibrium position, thereby creating an empty space. On heating the ions gain energy; hence the chance for formation of vacancies increases, yielding an increasing vacancy concentration. Vacancy formation is thus a thermally activated process. However, the number of vacancies remains small. Close to the melting point of a metal a typical value for the vacancy concentration is about 0.01 - 0.1%. Only one in 1,000 - 10,000 atom positions in the lattice is unoccupied.

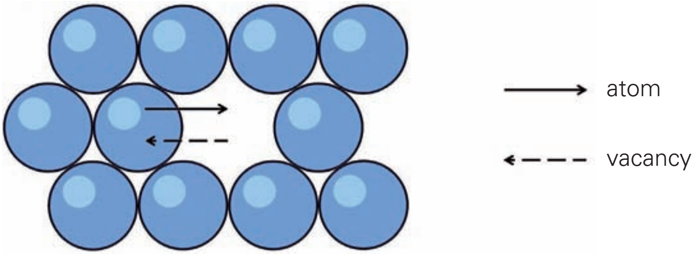


Figure 3.18. Direction of motion of a vacancy.

Problem 3.4 *Verify (see Figure 3.18) that a vacancy moves in a direction opposite to the motion of the atoms creating that vacancy.*

Vacancies play an important role in the diffusion occurring in crystalline solid solutions. Different metal ions can occupy the positions in the lattice. Such an assembly is called a substitutional solid solution. For example, if only a few B ions are dissolved in a crystal formed by A ions, the lattice will be the same as that of the pure A metal. The B ions can then move *via* vacancy formation. In case the B ions are substantially smaller than the A ions an interstitial solid solution can be formed where the B ions occupy the interatomic cavities of the A lattice. The interstitially dissolved B ions can diffuse *via* these interatomic cavities without requiring the formation of vacancies. As a rule it can be said that the diffusion of interstitially dissolved atoms is faster than that of substitutionally dissolved atoms. The atoms of carbon and nitrogen are much smaller than the atoms of iron, so to a certain extent carbon and nitrogen can be dissolved interstitially in iron. The atoms of chromium are of comparable size to the iron atoms, so chromium is dissolved substitutionally in iron. Based on this it can be expected that the diffusion of carbon in iron is much faster than the diffusion of chromium. The rate of many transformations in metals, *e.g.* precipitation (see Section 6.2) is strongly related to the diffusion rates of the atoms involved.

Linear defects or dislocations

Solidification or deformation can result in local shifts of lattice planes. These local distortions are described by dislocation lines. There are two types of dislocations: edge and screw dislocations. Figure 3.19 represents an edge dislocation. Edge dislocations can arise during crystal growth if a small orientation difference is present between the different parts of the growing crystal (see Figure 3.20).

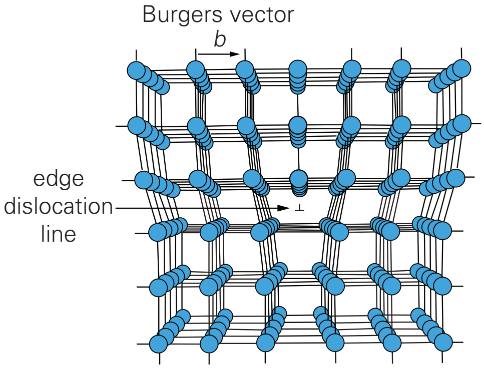


Figure 3.19. An edge dislocation.

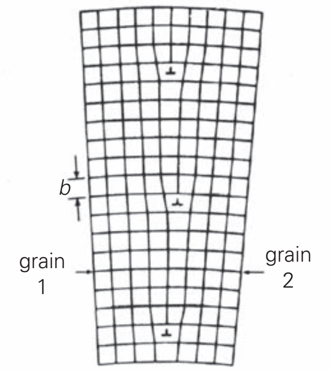


Figure 3.20. Small orientation differences lead to edge dislocations.

A screw dislocation is shown in Figure 3.21. Such a dislocation can also be represented as a spiral (Figure 3.22). Dislocations can move along certain crystallographic planes, so-called slip planes. Once a dislocation has passed through a crystal, slip has occurred over an atomic distance. This distance is called the Burgers vector *b* of the dislocation. For an edge dislocation the Burgers vector is perpendicular to the dislocation line, whereas for a screw dislocation the Burgers vector is parallel to the dislocation line (see Figures 3.19 and 3.21). Figure 3.23 shows the formation of dislocations resulting from partial slipping along lattice planes. An edge dislocation, a screw dislocation and a mixed dislocation are shown. Plastic deformation always implies slip along lattice planes and therefore this gives rise to the formation of dislocations. An increase of temperature can cause an annihilation of the dislocations formed, due to the increased mobility of the atoms. On cold deformation such annihilation does not occur. Hence, cold deformation can be defined as a deformation that causes an increase of the number of dislocations. It will appear that such an increase of the number of dislocations has a severe impact on the mechanical properties of the metal.

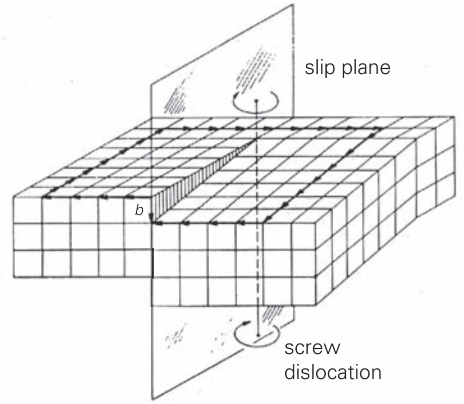


Figure 3.21. A screw dislocation.

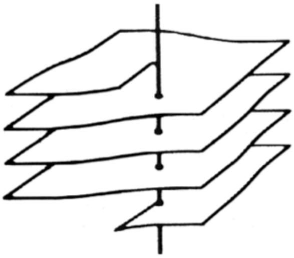
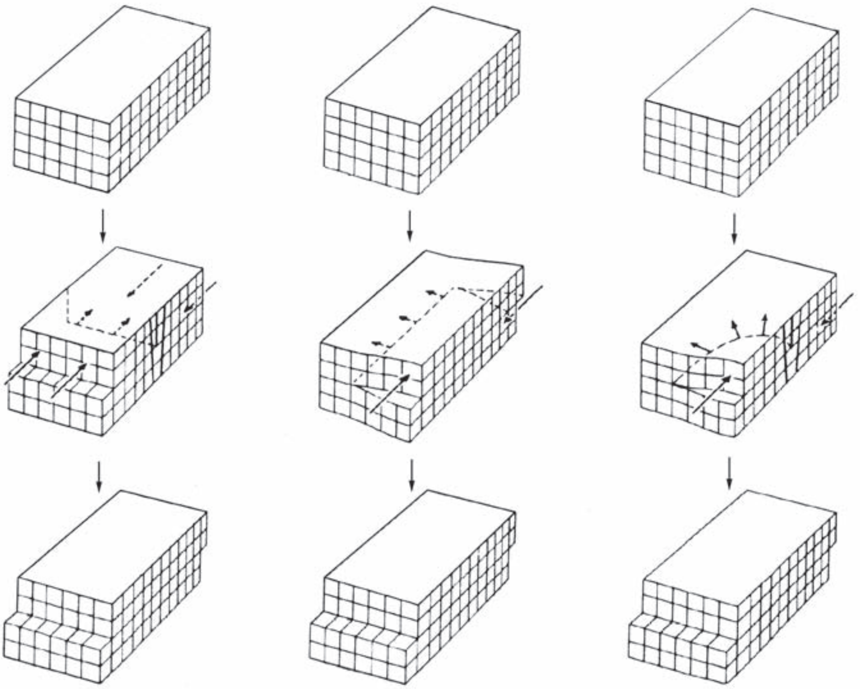


Figure 3.22. The spiral structure of a screw dislocation.

Plane defects

A metallic crystal has boundaries defined by planes. Those planes may be the metal surface itself or they can be the interface with another crystal. Compared to the lattice of the metal the interfaces locally show imperfect order. Engineering metals usually consist of a rather large number of crystals or grains; such metals are polycrystalline. The grain size usually varies between 0.01 and 1 mm. It depends on the thickness of the metal object whether or not the grain size is considered as large or small. For example, take the cigar tin of Figure 3.24. The thickness of the sheet metal forming this tin is about 0.2 mm, so in the direction perpendicular to the bottom, *i.e.* in the thickness direction, only a few grains will be present.



edge dislocation screw dislocation mixed dislocation

Figure 3.23. Dislocations caused by slip along lattice planes.

Figure 3.24. Cigar tin (photo: Louise van Mourik).

A metal's free electrons are able to cross over the grain boundaries. By virtue of this boundary crossing a piece of metal, despite having a large number of grains, shows remarkable cohesion, the individual grains stick together much more firmly than grains of sand on a beach. The number of neighbouring atoms in the vicinity of a grain boundary is smaller than in the bulk of the crystal grain. This implies a different energy state and therefore chemical corrosion in the region of the grain boundary is easier than for the central part of the grain. This phenomenon is applied in the etching of a metal surface to make the grain boundaries visible under an optical microscope.

From the discussion on the structure of crystal lattices, it can be deduced that the atom packing factor depends on the direction taken in the lattice. This is true for all crystal lattices. In a metallic crystal, atoms perform vibrations around equilibrium positions. The metallic bonding can be represented by elastic springs between the metal atoms. It can be expected that the elastic constants like the E-modulus depend on the interatomic distances. Suppose a bar with cross-section A is loaded in tension (see Figures 3.25 and 3.26). The elastic strain present is given by $\varepsilon = \Delta L / L_0$ corresponding to an internal stress of $\sigma = F/A$, where F is the applied load. The E-modulus is given by $E = \sigma/\varepsilon$. Suppose the metal concerned has a simple cubic lattice and the load F acts perpendicular to the cross-section. Without any loading, the lattice parameter equals r_0. The cross-section accounts for A/r_0^2 atoms and each atom experiences a force dF:

$$\mathrm{d}F = \frac{\sigma A}{A / r_0^2} = \sigma r_0^2 \tag{3.1}$$

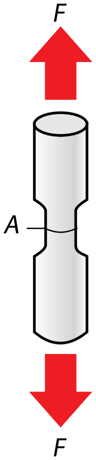


Figure 3.25. A tensile test bar with cross-section A.

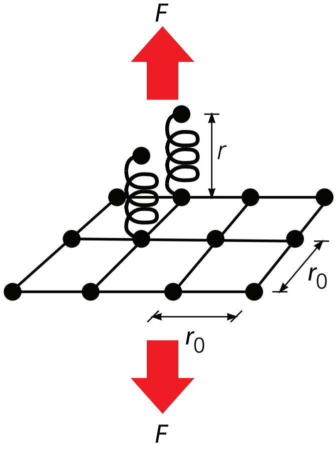


Figure 3.26. A spring model for metal atoms.

Supposing that the strain is evenly distributed along the length of the bar, it holds for the strain:

$$\varepsilon = \frac{\mathrm{d}r}{\mathrm{d}r_0}$$

The E-modulus can now be written as:

$$E = \frac{\sigma}{\varepsilon} = \frac{\mathrm{d}F}{r_0^2}\frac{r_0}{\mathrm{d}r} = \frac{1}{r_0}\frac{\mathrm{d}F}{\mathrm{d}r} \tag{3.2}$$

Where $\mathrm{d}F/\mathrm{d}r$ represents atomic interaction forces. Equation (3.2) makes it plausible that the value of the E-modulus depends on these interaction forces and on the interatomic distances (this example was given by Newey *et al.* (1990)).

In a polycrystalline metal with random orientation of the individual grains, the values of various properties will be an average of the values along the different lattice directions. A decreasing number of grains generally corresponds to an increasing grain size. Then the chance that the value of a property like the E-modulus in a certain direction deviates from the average will increase. As a consequence the values of mechanical properties may depend on the direction of measurement or on the direction of processing.

3.3.3 The reinforcement of metals and alloys

All metals – including metal alloys – contain dislocations. The presence of dislocations is very important for the mechanical properties of metals. The movement of a dislocation through a crystal yields slip along the so-called slip plane over one atomic distance (see Figure 3.21). Moving a dislocation requires much less force than is required to shear the crystal as a whole, just as it is much easier to move a fold in a carpet than to shift the whole carpet along the floor. Metals without any dislocations would require much more energy to be deformed and, as a consequence, should be much stronger. Metals do have dislocations, and therefore hindering the movement of dislocations is an effective method to increase the strength. As a matter of fact, hindering the movement of dislocations is the *only* way to increase the strength of metals.

For a metal with a given crystal lattice, there are four ways to hinder the movement of dislocations (these four ways are all applied to aluminium alloys; see Section 6.2):

1.	introduction of new dislocations	(*strain hardening*)
2.	decreasing the average grain size	(*recrystallization*)
3.	introduction of other atoms	(*solid solution hardening*)
4.	introduction of particles	(*precipitation*)

Strain hardening

The BCC and FCC lattices provide ample possibilities for movement of dislocations (see Section 10.2.3). However, the movement of dislocations always requires energy. As the lattice planes around a dislocation are somewhat deformed a field of elastic stresses is generated around a dislocation. In fact dislocations show mutual interactions *via* these elastic stresses. It has been found that these interactions effectively hinder the movement of individual dislocations. At low temperatures, external forces are the main cause for the motion of dislocations. These forces cause slip along slip planes of the crystal, giving rise to the creation of new dislocations. These new dislocations hinder further movement of dislocations *via* the local stresses. Therefore a metal that is being deformed at low temperatures undergoes hardening. This phenomenon is called strain hardening. The strain hardening during cold deformation of non-alloy soft steel and of (commercially) pure aluminium is of industrial importance. Table 3.3 and Figure 3.27 illustrate the strain hardening of commercially pure aluminium in terms of some mechanical properties.

Table 3.3. Strength of cold deformed commercially pure Al99.5.

condition	*yield strength* [*MPa*]	*ultimate tensile strength* [*MPa*]	*fracture strain* [*%*]
soft	10 - 20	70 - 80	50 - 60
1/4 hard	40	100	10
1/2 hard	70	120	7
3/4 hard	130	150	4 - 5
hard	175	180	2 - 3

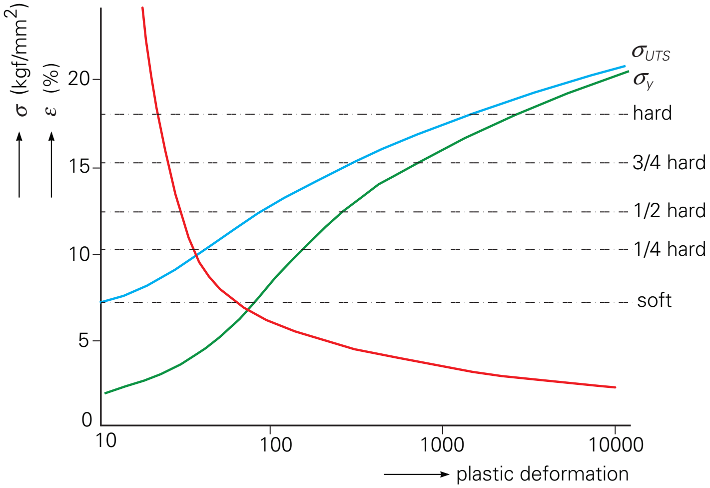


Figure 3.27. Strain hardening of Al99.5 as a function of the plastic deformation $(A_0–A)/A \times 100\%$, with A_0 the original cross-sectional area.

Problem 3.5 *What is the relationship between the units for the strength in Figure 3.27 and Table 3.3?*

Recrystallization and recovery

Strain hardening results in a loss of deformability and the metal finally even cracks. The effect of strain hardening, except for possible cracks, can be removed by annealing, *i.e.* by increasing the temperature. Above a certain temperature, the atomic mobility increases such that dislocations start to move through the crystal. It should be noted that mobility of vacancies is related to the mobility of dislocations. The state with the increased number of dislocations is thermodynamically not stable: each dislocation represents an excess amount of elastic energy. The reduction of this elastic energy is the driving force for the annihilation of dislocations at a sufficiently high temperature.

Recovery is the term used to describe the decrease of elastic energy *via* rearrangement and annihilation of the dislocations. The remaining dislocations tend to form more or less regular patterns to further reduce the elastic stresses, thus yielding an overall decrease of elastic energy. When the internal stresses become weaker, the hardness is reduced and the deformability of the metal is recovered. The temperature where this happens is called the recovery temperature, T_{rec}. The value of T_{rec} is about equal to 0.3 T_m where T_m is the melting point in Kelvin. Note that on recovery, the *morphology of the metal grains does not change*.

Recrystallization implies a change of the shape and size of the metal grains. The decrease of the number of dislocations is achieved by the formation of new crystal grains and the disappearance of old ones. The new grains contain much less dislocations, which causes a large decrease in hardness (see Figure 3.28). The grain size after recrystallization also depends on the preceding cold deformation: the larger the cold deformation, the smaller the grain size after recrystallization.

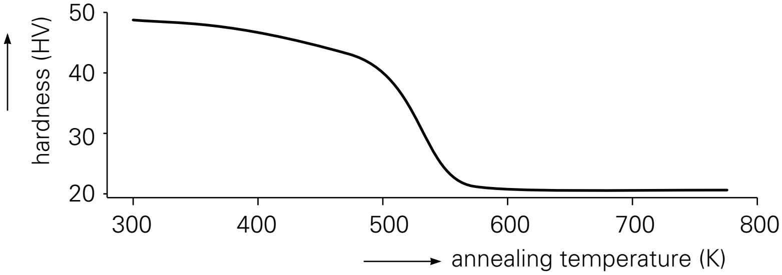


Figure 3.28. The hardness of aluminium (cold deformation 72%) as a function of temperature of annealing for a fixed time (Weidmann et al. (1994)).

Recrystallization proceeds *via* the nucleation of new grains and subsequent grain growth. Below a critical deformation no nucleation will take place and recrystallization will not occur. After successful nucleation grain growth will proceed until the newly formed grains touch each other. Then recrystallization is completed and continued annealing will only result in the growth of large grains at the expense of the smaller ones. For most metals the critical deformation for recrystallization to occur is in the order of 0.02, or 2%. It is reasonable to expect that the temperature of recrystallization, $T_{recryst}$, is higher than T_{rec}. Indeed, in terms of the melting point in Kelvin the value of $T_{recryst}$ is about 0.4 - 0.5 T_m. On annealing below $T_{recryst}$ and below the critical deformation only recovery occurs. A strong grain growth can occur after deformation just above the critical deformation and subsequent annealing at the recrystallization temperature. The value of $T_{recryst}$ cannot be defined with great accuracy. It depends on the history of the metal, its composition, and of course on the previously applied deformation.

It is now possible to distinguish between cold and hot deformation. Cold deformation involves deformation below T_{rec} and hot deformation above T_{rec}. Cold deformation always implies strain hardening. Hot deformation implies that there is the possibility for recovery. It is common practice to perform hot deformation above the recrystallization temperature. Examples of hot deformation are hot rolling and hot extrusion.

Large grains can cause development of a very rough product surface like an orange peel during subsequent cold deformation. Metal alloys intended to undergo cold deformation should have small grain sizes to prevent this. Note the small number of grains in the cross-section of a cigar tin or a beverage can! The desired grain size results from choosing the right combination of preceding cold deformation and recrystallization and annealing conditions (time and temperature). Recrystallization may even result in a decreased grain size providing an increased strength. The strength of a metal is reciprocally related to the grain size *via* the Hall-Petch relation:

$$\sigma_y = \sigma_0 + \frac{k}{\sqrt{d}} \tag{3.3}$$

Where σ_y is the yield strength, σ_0 and k are constants depending on the metal alloy concerned, and d is the average grain diameter. The grain boundaries act as barriers for the movement of dislocations and as such are a source of strength. After recrystallization, a new cold deformation may be used to determine the ultimate and desired level of strength.

Solid solution hardening

Alloying atoms in solid solution (the ‘solute’ atoms) generally have a different size compared to the atoms of the solvent, also called the host metal. An alloying atom on an atomic position in the lattice of the host metal causes elastic lattice stresses. The interaction with the elastic stress fields around dislocations then causes additional hindering of the dislocation mobility and hence an increase of strength. This effect only occurs if the alloying atoms remain in solid solution.

Precipitation hardening

The fourth possibility to increase strength is precipitation or age hardening. Precipitation here means precipitation from a supersaturated solid solution. Many metal alloys show a decreasing solid solubility with decreasing temperature (see Section 4.3). A supersaturated solid solution can easily be obtained by first heating the alloy with a suitably chosen composition to an elevated temperature where the alloying element is present in a solid solution. Quenching to low temperatures then prevents the precipitation to occur, yielding a supersaturated and therefore unstable solid solution at these low temperatures. A limited temperature increase (ageing) then provides the opportunity for precipitation of the alloying atoms into small particles with a structure different from the host metal structure. These precipitates as formed in precipitation hardening act as barriers for the movement of dislocations and cause an increase in strength of the alloy. So, a *necessary* condition for precipitation hardening is the decreasing solid solubility, but this is not the *sufficient* condition for a practically useful precipitation process. The attainable improvement of the mechanical properties should be worthwhile. The phenomenon is important for aluminium alloys and will be studied in more detail in Section 6.2.

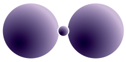
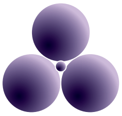
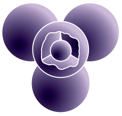
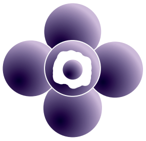
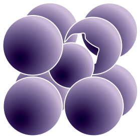
3.4 Ceramics

Generally, ceramics are crystalline inorganic compounds or combinations of compounds of (mainly) metals and non-metals. Ceramics usually possess high hardness values, indicating primary bonding. The lattices of crystalline ceramic compounds are similar to those of metals, but the occupation with atoms and/or ions is much more complicated. The primary bonding in ceramics is mainly covalent, ionic or a mixture of covalent and ionic. Table 3.4 presents some examples.

Table 3.4. Bonding in compounds (Anderson et al. (1991)).

compound	*bonding*	*compound*	*bonding*	*compound*	*bonding*
Si	covalent	NaCl	ionic	Al_2O_3	covalent-ionic
SiC	covalent	MgO	ionic	SiO_2	covalent-ionic
Si_3N_4	covalent	mica	ionic	window glass	covalent-ionic

Table 3.5. Structural parameters for stable ceramics (Callister (2008)).

coordination number	*ratio of radii cation/anion*	*coordination geometry*
2	< 0.16	
3	0.16 – 0.23	
4	0.23 – 0.41	
6	0.41 – 0.73	
8	0.73 – 1.0	

In the ionic bonding, the metals take the position of the positive ions (cations) and the non-metals take the position of the negative ions (anions). Generally, the cations are smaller than the anions. Obviously, the cations try to surround themselves with as many anions as possible, and *vice versa*. Stable ceramic compounds can be formed when the anions surrounding a cation are all in direct contact with that cation. The coordination number indicates the number of anions in direct contact with the cation. In fact this number is determined by the ratio of the radii of the cations and anions. So, the coordination number and this ratio are important parameters to describe stable ceramic crystal structures (see Table 3.5). Cations are mostly designated with a capital from the beginning of the alphabet and the anions with a letter from the end. A species of ceramics can then be described with combinations of such capitals. This section pays attention to the structural types AX, A_nX_p en $A_mB_nX_p$.

AX

A large number of ceramics consist of equal numbers of cations and anions: AX. In this group the following crystal structures are of practical importance. Each of the species is named after a characteristic example with that particular crystal structure.

Name of the crystal structure: rock salt

The most common example is common salt: NaCl, also known as rock salt. Figure 3.29 schematically shows the positions of the sodium and chlorine ions.

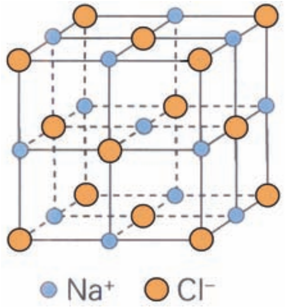


Figure 3.29. The arrangement of the sodium and chlorine ions in NaCl.

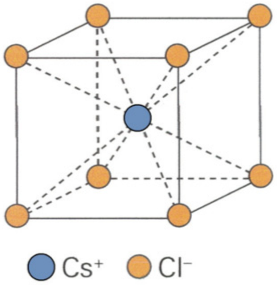


Figure 3.30. The arrangement of the caesium and chlorine ions in CsCl.

Problem 3.6 *1. Verify that the sodium and chlorine ions occupy atom positions of an FCC lattice.*

2. Determine the coordination number of the lattice of Figure 3.29.

Name of the crystal structure: caesium chloride

Figure 3.30 schematically shows the positions of the caesium and chlorine ions.

Problem 3.7 *1. Check whether or not the lattice in Figure 3.30 is a BCC lattice.*

2. Determine the coordination number for the lattice in Figure 3.30.

Name of the crystal structure: zinc blende

Zinc blende is a compound of zinc and sulphur. Its bonding is predominantly covalent. Figure 3.31 schematically shows the positions of the zinc and sulphur atoms. Each zinc atom is connected with four sulphur atoms and *vice versa*. In most cases, the bonding for the zinc blende type of crystal structure is covalent. Zinc telluride and silicon carbide also show the zinc blende lattice.

A_nX_p

For this class of compounds the charge of the cation is not equal to the charge of the anion. An example is calcium fluoride, CaF_2 (mineral fluorite). Figure 3.32 shows schematically the arrangement of the calcium and fluorine ions.

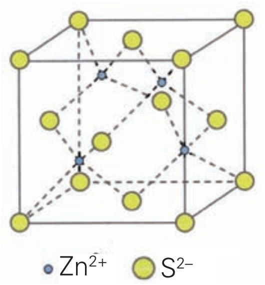


Figure 3.31. The arrangement of the zinc and the sulphur ions in zinc blende.

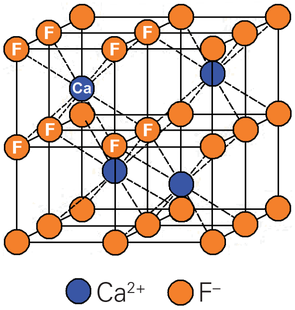


Figure 3.32. The arrangement of the calcium and fluorine ions in CaF_2.

Problem 3.8 *Describe two similarities between the CsCl and the CaF_2 lattice.*

$A_mB_nX_p$

This type has two different cations and one species of anions. An example is barium titanate, $BaTiO_3$. At temperatures above 120°C the ions are arranged as shown in Figure 3.33. This structure is known as the perovskite structure.

Table 3.6 provides an overview of the crystal structures for some ceramics.

Table 3.6. Crystal structures of some ceramics (Callister (2008)).

name structure	structure	anion packing	coordination number		examples
			cation	anion	
rock salt	AX	FCC	6	6	NaCl, MgO, FeO
caesium chloride	AX	cubic	8	8	CsCl
zinc blende	AX	FCC	4	4	ZnS, SiC
fluorite	AX_2	cubic	8	4	CaF_2, UO_2, ThO_2
perovskite	ABX_3	FCC	A: 12; B: 6	6	$BaTiO_3$, $SrZrO_3$
spinel	AB_2X_4	FCC	A: 4; B: 6	4	$MgAl_2O_4$, $FeAl_2O_4$

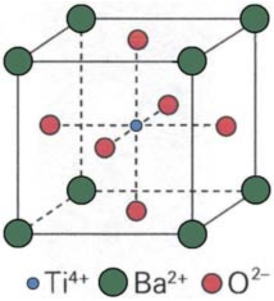


Figure 3.33. The arrangement of the ions in barium titanate.

Most ceramic compounds are crystalline, but also non-crystalline or amorphous ceramic compounds may occur and these constitute a rather important class of materials. A common example of an amorphous ceramic is window glass. Silica, SiO_2, is the main constituent of window glass and it can have the crystalline or the amorphous state. On cooling slowly from the liquid state, the crystallization of SiO_2 starts at a certain temperature T_m, analogously to the solidification of a metal (see Figure 3.34). A sufficient increase of the cooling rate causes suppression of the solidification *via* crystallization: the liquid becomes supercooled. The supercooled liquid then becomes a solid at the so-called glass transition temperature, T_g. This amorphous form of solid is called a glass. The glass transition temperature is difficult to define exactly and its value also depends on the applied cooling rate. By using a range of cooling rates it is found that an increase of the cooling rate increases the value of T_g (see Figure 3.34, right). On an atomic level, the glassy state is characterized by a rather open network of the participating atoms or groups of atoms (see Figure 3.35). This open network provides space for other atoms allowing the properties of the glass to be influenced. The structure of a glass can be transformed, as the amorphous glass is not thermodynamically stable. For example heat treatment can result, at least partly, in the formation of the crystalline state. The resulting substance is called a glass ceramic. This process is called devitrification and it finds application in some consumer products: glass ceramic cooking plates form an example. Particles present in the glass may induce spontaneous devitrification under certain conditions, the transparency then slowly fades due to the formation of crystalline regions in the substance.

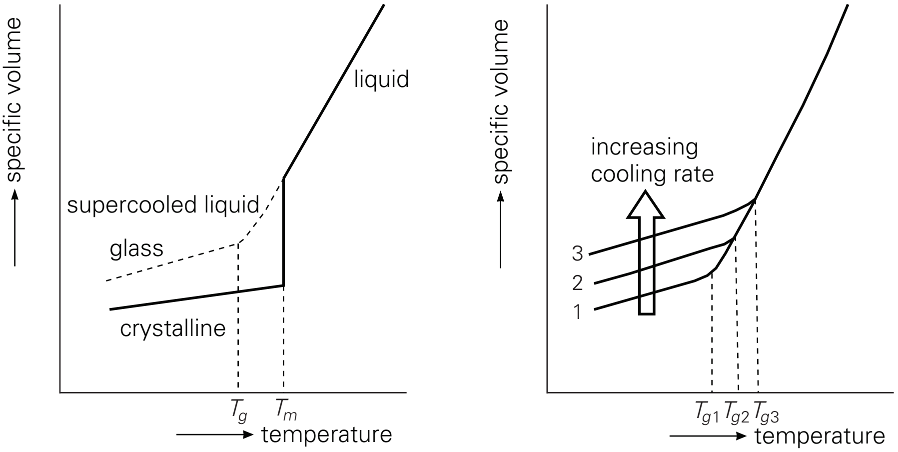


Figure 3.34. The specific volume of silicon dioxide as a function of temperature.

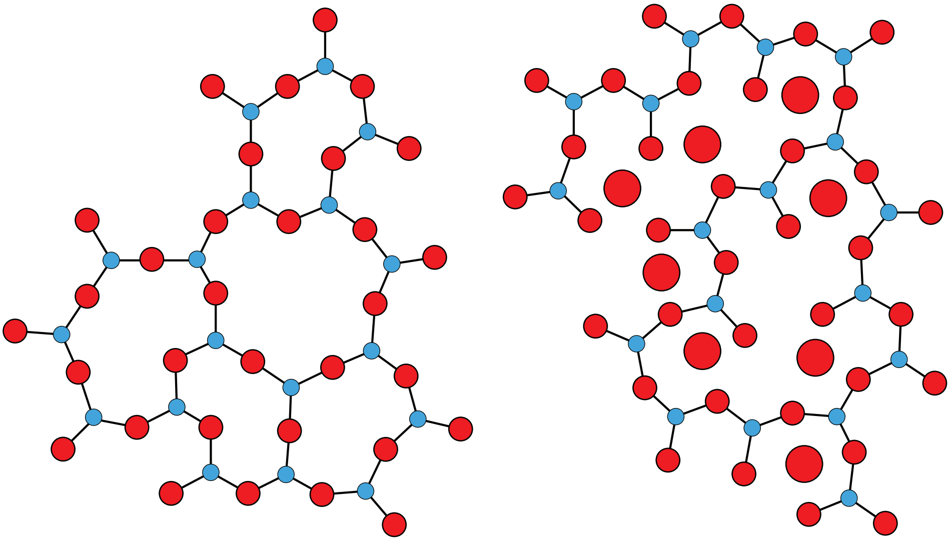


Figure 3.35. Networks in the glassy state.

Problem 3.9 *The representation of the basic network in Figure 3.35 consists of blue dots and red circles. Indicate the silicon and the oxygen atoms.*

The ceramics encountered in practice do not have the perfect crystal lattices described above. The observed deviations are called defects, just like in metals. This section deals only with point defects and dislocations. Point defects can of course occur in the lattices of the cations and of the anions. In any case electrical neutrality must be maintained. The point defects include vacancies and interstitially dissolved ions. To simplify the discussion in the following we will only consider AX compounds (see Figure 3.36).

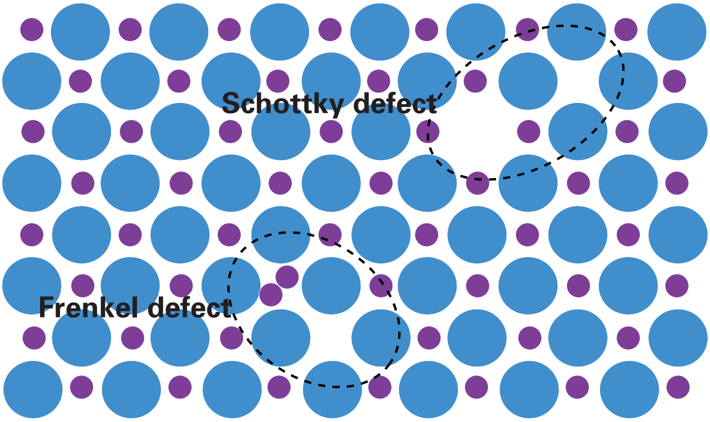


Figure 3.36. Schematic representation of a Frenkel and a Schottky defect (Callister (2008)).

A cation vacancy and a cation interstitial (see Figure 3.37) form a Frenkel defect.

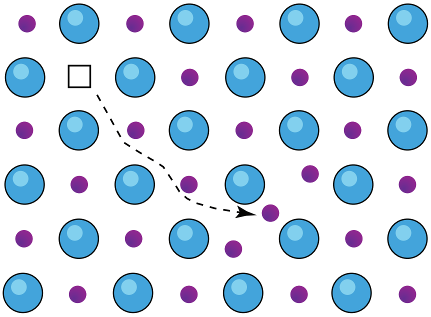


Figure 3.37. The development of a Frenkel defect.

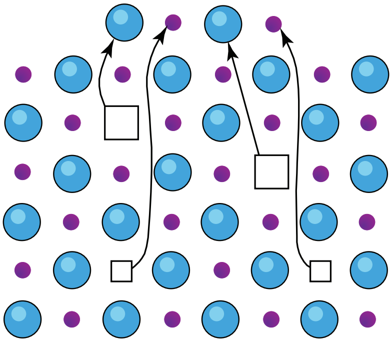


Figure 3.38. The development of a Schottky defect.

The Schottky defect consists of a cation vacancy and an anion vacancy (see Figure 3.38). Note that the ratio between cations and anions does not change, electrical neutrality is always maintained. Some ions can possess different valencies. For example, the iron cation can be 2+ as well as 3+. A Fe^{2+} ion vacancy can compensate for the presence of two Fe^{3+} ions to maintain electrical neutrality. Hence, iron oxide occurs with a wide range of compositions, often written as $Fe_{1-x}O$, with $\frac{2}{3} < x < 1$.

Impurities are frequently present in ceramic compounds. The atoms and ions of these impurities can dissolve interstitially as well as substitutionally, depending on their relative size. The substitutionally dissolved ion can be cationic or anionic. As always, electrical neutrality must be maintained, by the formation of the defects mentioned above.

Like metals, crystalline ceramics possess dislocations. Unfortunately, plastic deformation *via* movement of dislocations is virtually impossible in ceramics as slip along lattice planes is hindered in the vast majority of ceramics. It should be noted that slip implies the disturbance of the negative surrounding of the positive ions and *vice versa*. This gives rise to large repulsive forces and effectively prevents the occurrence of slip (see Anderson *et al*. (1991) and Callister (2008)). For amorphous ceramic compounds plastic deformation might be possible by moving the separate molecules or networks. However, again due to the strong bonding forces, the shape stability of amorphous ceramics is very great. Hence, the possibilities for plastic deformation of amorphous ceramics are also very limited. Glass shows brittle fracture at room temperature but with increasing temperature the possibilities for plastic deformation are enhanced. Glass blowing occurs in the vicinity of the glass transition temperature (see also Section 10.4).

Ceramic materials can be obtained by a large number of techniques (see Van der Put (1998)). Each technique offers a broad range of processing conditions. These processing conditions have a major effect on the structural characteristics of the obtained ceramic. As is the case with metals and metal alloys the grain size of a ceramic is an important feature. Other common structural features of ceramics are pores and flaws. The grain size, the pore fraction and the number of flaws are strongly related to the applied processing routes. These three features also directly influence the properties of ceramics (see Chapter 9). With many ceramics the applied manufacturing route coincides with the material formation itself (*e.g.* the material of a brick is formed during brick manufacturing). As a consequence of this, ceramics are characterized by very strong interactions between the corners of the **PMM** triangle (see Figure 3.1).

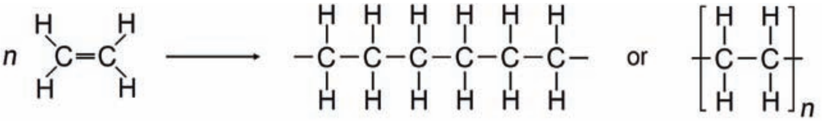
3.5 Polymers

3.5.1 The structure of polymers

Synthetic organic polymers are without any doubt the most applied new materials of the last century. On a molecular level the main characteristic of a polymer is the very high molecular weight, in the order of 10^4 - 10^6 g/mole. Therefore these substances are called high-molecular substances. Low-molecular mass substances have molecular weights in the order of 10^2 g/mole. (*Since we are dealing with masses rather than weights 'molecular mass' or, even better, 'molar mass' would be more appropriate terms. However, in polymer literature 'molecular weight' is commonly used, and therefore this term will also be used in this book*).

It should be noted that commonly used plastics consist of polymers with often one or more additives. The other component may be another polymer, as in a polymer blend, but also non-polymeric compounds are added.

Synthetic organic polymers are formed from low-molecular weight monomers. These monomers are connected in a chain-like manner by covalent bonds. In some cases the polymer chains may be branched. For an important class of polymers, like the polyolefins, the monomer is unsaturated; it contains a double bond that opens on polymerization and connects to another monomer, thus forming a long chain. The simplest example is the formation of polyethylene from the ethylene monomer:



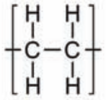
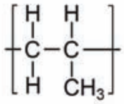
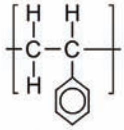
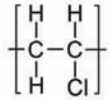
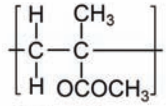
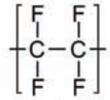
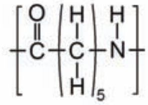
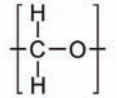
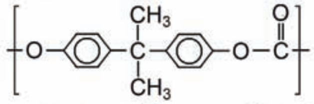
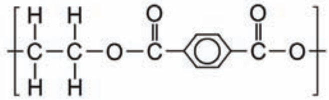
The last representation is a shorthand notation for the polymer chain molecule. One can ask oneself the question how large *n*, the so-called polymerization number or degree of polymerization, should be before one can speak of the *polymer* polyethylene (see Table 3.7).

Table 3.7. Chain formation of ethylene.

n	*compound*	*melting temperature* [°C]
1	ethane	–172
2	butane	–135
4	n-octane	–57
200	polyethylene	+130

Above a critical value of *n* (in this case in the order of *n* = 200) the chain length has hardly any influence on properties such as the melting temperature. Chain formation can also occur using monomers without double bonds but in all simple polymer chains one can find a repeat unit. Such polymers are called *homopolymers*. It is also possible to polymerize two or more different monomer types together into one polymer chain, and these are called *copolymers*. Table 3.8 gives an overview of the more common polymers.

Table 3.8. Some important polymers and their repeat units.

polymer	abbreviation	repeat unit
polyethylene	PE	
polypropylene	PP	
polystyrene	PS	
polyvinyl chloride	PVC	
polymethyl methacrylate	PMMA	
polytetrafluoroethylene	PTFE	
polyamide (nylon-6)	PA (PA-6)	
polyoxymethylene	POM	
polyethylene terephtalate	PET	
polycarbonate	PC	

In polymeric materials the chains can be present as single chains. It is also possible that the chains are interconnected to form networks. *Single chains* are often linear, although branches may occur. Polymer chains are very long compared to their cross-section. Their aspect ratio is roughly similar to a human hair of about 0.1 - 1 meters length. Usually, these chains are not stretched, but they form random coils, which are highly entangled with each other. Between the separate chains only Van der Waals bonds, and sometimes hydrogen bonds, exist and as a result polymers usually have low values of the E-modulus. In addition the entanglement of the chains hinders flow. Therefore, they possess a high viscosity in the liquid state, and shaping *via* the viscous molten state requires a lot of energy. In *networks* the chains are interconnected in a covalent way, cross-linked to one another. Such a polymer network is in essence a single giant molecule. On the basis of the structures described above, polymers can be divided into three main categories:

1. *Thermoplastics* consist of single chain polymer molecules and they soften when heated (and eventually liquefy). They regain their solid state on cooling.
2. *Rubbers* also contain single chains, but these are cross-linked by covalent bonds (by vulcanization, see Section 7.4). In this way networks are formed; such a network is in essence a giant molecule: one molecule for each car tyre.
3. *Thermosets* also consist of networks of chains, but the cross-link density is very high. These networks are often formed through a chemical reaction at higher temperatures.

Table 3.9. Some important polymers.

abbreviation	*name*	*description*
1. thermoplastics		
PE	polyethylene	fairly soft and tough
PP	polypropylene	stronger than PE
PVC	polyvinyl chloride	hard and tough
PS	polystyrene	hard and brittle
PMMA	polymethyl methacrylate	hard, highly transparent
PTFE	polytetrafluoroethylene	chemically resistant, mechanically weak
2. rubbers		
SBR	styrene-butadiene rubber	wear resistant
PIB	polyisobutylene	gas-tight
3. thermosets		
PF	phenolic resin	Bakelite®, hard
UF	ureum formaldehyde resin	colourless, high surface gloss
UP	unsaturated polyester	clear, mostly with glass filler

The classification is based on the number of bonds between the chains. In thermoplastics no covalent connections between the chains are present, in rubbers a certain number of cross-links is necessary to prevent permanent deformation, in thermosets the number of cross-links is much higher, resulting in a rigid network. A thermoset, once formed, will soften a little on heating, but it will not liquefy. Table 3.9 describes some important polymers.

3.5.2 Chain structure

A linear polymer chain consists of a backbone to which side groups are attached. These side groups partly determine the name of the polymer in question. They also determine to a large extent the properties of the polymer. *Copolymers* are composed of two or more different monomer types. Some common copolymers are given in Table 3.10.

Table 3.10. Copolymers.

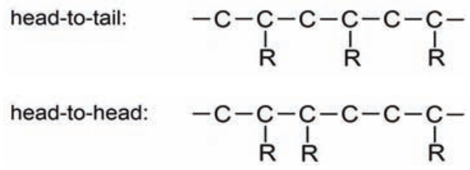
name	*copolymer type*	*monomers*
ABS	terpolymer	acrylonitrile + butadiene + styrene
SAN	dipolymer	styrene + acrylonitrile
EPR	dipolymer	ethylene + propylene
SBR or SBS	dipolymer	styrene + butadiene
IIR	dipolymer	isobutylene + isoprene
EPDM	terpolymer	ethylene + propylene + a diene

Generally speaking, polymer chains exhibit a high degree of regularity. However, variations are possible in:

i. monomer arrangement
ii. position of side groups (stereoisomerism)
iii. configuration around a double bond (geometrical isomerism)
iv. chain branches
v. copolymer structures.

i. Monomer arrangement

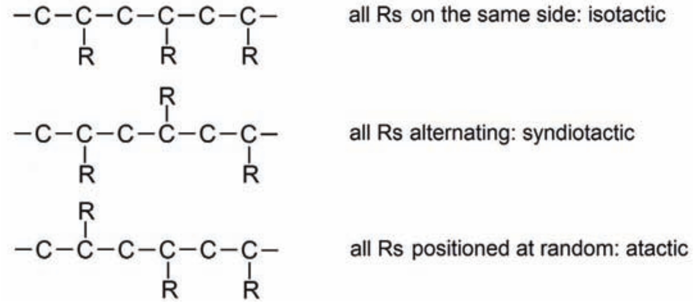
Monomers can be linked to each other in a ‘head-to-tail’ configuration or, alternatively, in a ‘head-to-head’ configuration. In most cases the head-to-tail configuration predominates. Both cases are illustrated below for a vinyl polymer, *i.e.* a polymer obtained by polymerization of the unsaturated vinyl compound CH_2=CHR:



(*Note: In the schematic representation of polymer structures the hydrogen atoms are usually not shown, contrary to all other groups which are always indicated*).

ii. Position of side groups (stereoisomerism)

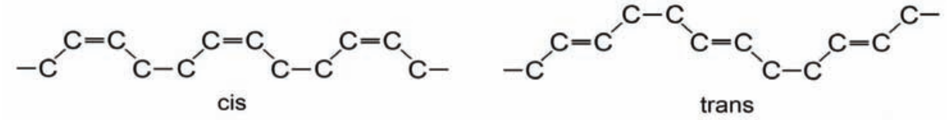
In chains of the type $–CH_2–CHR–CH_2–CHR–CH_2–CHR–$ the side groups can be distributed along the chain in a regular or irregular way.



In most polymerization processes predominantly atactic chains are formed. For the manufacture of isotactic and syndiotactic polymers special stereospecific polymerization processes are available. By such a method isotactic polypropylene is produced. Atactic polypropylene is useless for applications.

iii. Configuration around a double bond (geometrical isomerism)

A double bond cannot rotate around its axis, therefore two different configurations can occur:



The cis and trans configurations of the same polymer strongly differ in properties. They are completely different materials. For example, natural rubber, cis-1,4-polyisoprene, clearly is an elastomer and gutta percha, the trans configuration, is a hard resinous thermoplastic substance at room temperature that softens around 60°C.

iv. Chain branches

Branches interfere with the regularity of the polymer chain when they are randomly distributed along the chain; see Figure 3.39. The number, length and positioning of the branches can have a major impact on both the mechanical properties and the processability of a polymer.

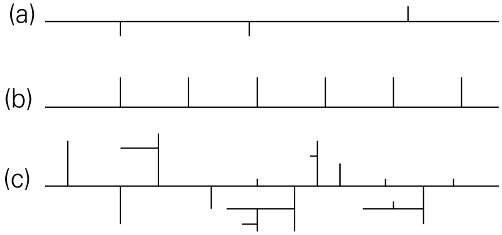


Figure 3.39. (a) Chain with few branches; (b) heavily branched chain, but regular; (c) heavily branched chain with irregular branches.

v. Copolymer structures

In a random copolymer the sequence of the monomers is, obviously, completely random:

—A—A—A—A—B—B—A—B—A—A—B—B—B—B—A—A—

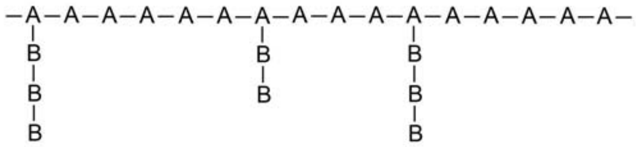
A more regular structure is found in alternating copolymers:

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

Regularity is also found in block copolymers:

—A—A—A—A—A—A—A—B—B—B—B—B—B—B—B—A—A—A—A—

and in graft copolymers:



$$\begin{array}{cccccccccccccccc} -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A & -A- \\ | &&&&&& | &&&& | &&&&& \\ B &&&&&& B &&&& B &&&&& \\ | &&&&&& | &&&& | &&&&& \\ B &&&&&& B &&&& B &&&&& \\ | &&&&&&&&&& | &&&&& \\ B &&&&&&&&&& B &&&&& \end{array}$$

All polymer chains are more or less flexible. The flexibility is determined by the possibilities for rotation around bonds along the backbone of the chain. All single bonds can rotate, double bonds between the C atoms are unable to rotate. In Table 3.11. a number of main chains is listed, the flexibility decreases from top to bottom. Side groups also influence the chain flexibility, be it in a secondary way; their influence is relatively more important as the main chain is more flexible. Interactions between the polymer chains take the form of secondary bonds like the Van der Waals bonds and hydrogen bonds (see Section 3.2). These secondary interactions together with the chain flexibility have a large effect on the temperature for the glass-rubber transition as well as the melting point of the polymer (see Section 3.5.3).

Table 3.11. Some polymer chains in decreasing order of flexibility.

characteristic part of the chain	*polymer*	*flexibility*
$-C-O-C-$	POM, polyoxymethylene	high
$-C-C-C-$	PE, polyethylene	
$-C-C-N-$	PA, polyamide (nylon)	
$-C=C-C-$	BR, butadiene rubber	
	PC, polycarbonate	low

3.5.3 Glassy state and glass-rubber transition

For most non-polymeric materials the solid phase is crystalline. On heating it transforms into the liquid phase at the melting temperature T_m. At this transition almost always both volume and heat content (due to the heat of fusion) increase. The volume change at T_m is illustrated in Figure 3.40, a crystalline material follows the line FCBA.

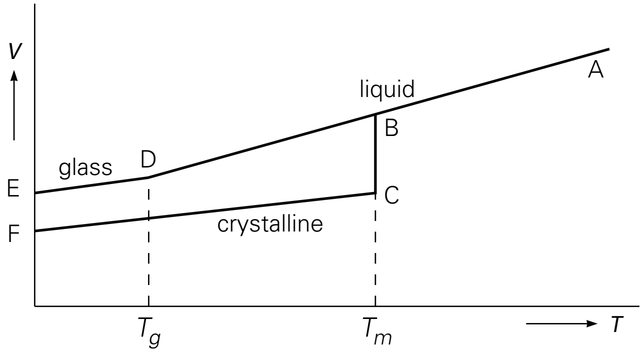


Figure 3.40. Specific volume as a function of temperature (Van der Vegt (2006)).

There are also materials that are unable to crystallize on cooling from the melt. At a certain temperature they solidify without a discontinuous change of volume, the liquid state is frozen in. Glass (see Section 3.4) is an example of such a material. The temperature at which a glass solidifies is called the glass transition temperature T_g (point D in Figure 3.40). Glassy materials are amorphous in the solid state.

Many polymers are also amorphous. In the amorphous state the chains are highly distorted, forming random coils of roughly spherical shape, which are highly entangled with one another. Amorphous polymers also follow the line EDBA in Figure 3.40 when the temperature is increased. At the glass transition temperature a polymer does not immediately transform from a glass into a free flowing liquid, instead it first transforms into a rubbery, elastic fluid. Therefore, for polymers this temperature is called the *glass-rubber transition* *temperature* T_g. On further heating the rubbery fluid gradually becomes a highly viscous liquid.

Another useful property to illustrate the behaviour of a thermoplastic in its different phases is the E-modulus, which determines the elastic behaviour of the material. This modulus is given as a function of temperature in Figure 3.41. After a decrease with a factor of thousand to ten thousand at T_g the polymer enters the rubber plateau, which extends to higher temperatures with increasing polymer chain length. In the rubbery state the ability to be deformed under an external load is determined by the possibility of deforming the entangled polymer coils. Under the influence of a tensile load untwisting and straightening of the chains occurs and as a result the coils are distorted from their spherical shape. After removing the external load the chains spring back to their original randomly coiled configuration and the polymer sample returns to its original shape: only elastic deformation has taken place. Of course this is only true if the load is not applied for too long, under prolonged loading permanent viscous flow will result. On heating to temperatures above the rubbery region the chains of a thermoplastic experience such a great freedom of movement that the thermoplastic becomes liquid-like and will begin to flow. This process starts at the flow temperature T_v and this is accompanied by a further decrease of the E-modulus.

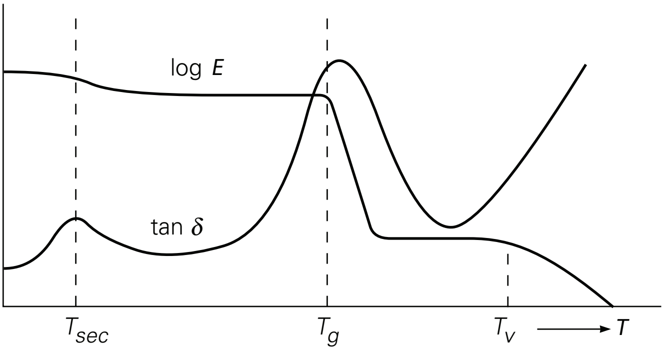
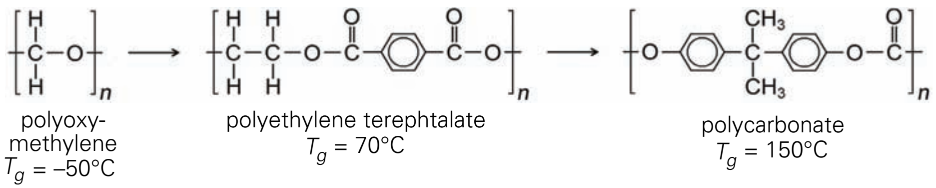
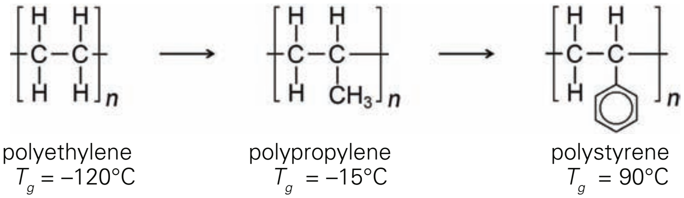


Figure 3.41. Log E and tan δ of an amorphous polymer as a function of temperature.

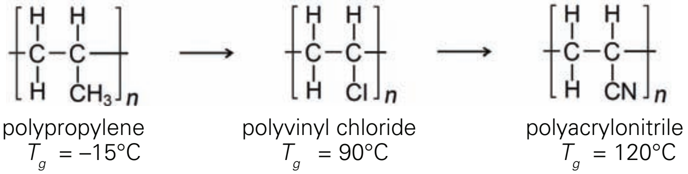
If a polymer shows glassy as well as crystalline behaviour, then the glassy state has a higher specific volume. This explains the distance between the curves ED and FC in Figure 3.40, the volume difference is the *free volume* V_f. Below T_g the free volume is nearly independent of temperature; above T_g, V_f increases rapidly with temperature. The free volume in the glassy state in some cases allows minor motions of small parts of the polymer chains or of side groups. At the temperature where the free volume is sufficient to allow such movement, a decrease of the E-modulus is found. Because this decrease is much smaller than that at T_g, these transitions in the glassy state are called *secondary transitions*. These transitions show up even more clearly in the mechanical damping. The *damping* or *loss factor* (tan δ) is a measure of the speed with which oscillations or vibrations are damped out. The damping exhibits a high maximum around T_g and a smaller maximum at a secondary transition, T_{sec} (see Figure 3.41). The secondary glass transitions are of great importance for the impact strength of a glassy polymer (see Section 7.3.2). They offer the possibility to absorb energy on impact: the polymer is less brittle and therefore has higher impact strength. An example of a secondary transition is that of PMMA at 25°C. At this temperature rotation of the $-COOCH_3$ side group (see Table 3.8) becomes possible. The position of T_g is determined by the flexibility of the polymer chains and by the attractive forces between the chains. The flexibility of a chain depends on the stiffness of the chain backbone and/or the presence of side groups. If at low temperatures rather large movements of parts of the chains are possible, then T_g is also low. The influence of increasing stiffness of the main chain is illustrated by the following series:



The presence of side groups reduces the flexibility of the main chain and thus side groups may increase chain stiffness. An example of this influence is given by the following series:



The influence of the interactions between the chain molecules on T_g is obvious: the stronger the interactions, the greater the mutual hindrance and the higher T_g. The following series demonstrates this effect clearly:

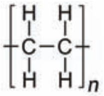


The side groups of the polymers of this series are nearly the same size, so the stiffness of the chain is almost the same. However, PP is non-polar, PVC has a dipole character and PAN has even stronger dipoles.

3.5.4 Semicrystalline polymers

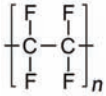
Not all thermoplastics are amorphous, a rather large number show crystallinity to some extent. A necessary condition for crystallization is a regular chain structure, that allows positioning of the chain molecules on a crystal lattice. Regular chains are found when:

i. The side groups on both sides of the main chain are equal and the chain is symmetric; examples are:



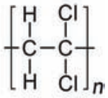
$$\left[\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}\right]_n$$

polyethylene (PE)



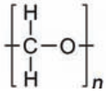
$$\left[\begin{array}{ccccc} & \mathrm{F} & & \mathrm{F} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{F} & & \mathrm{F} & \end{array}\right]_n$$

polytetrafluoroethylene (PTFE)



$$\left[\begin{array}{ccccc} & \mathrm{H} & & \mathrm{Cl} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & \mathrm{Cl} & \end{array}\right]_n$$

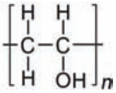
polyvinylidene chloride (PVDC)



$$\left[\begin{array}{ccccc} & \mathrm{H} & & & \\ & | & & & \\ - & \mathrm{C} & - & \mathrm{O} & - \\ & | & & & \\ & \mathrm{H} & & & \end{array}\right]_n$$

polyoxymethylene (POM)

ii. The chain is not symmetric, but the side groups are so small that they can fit into the interstitial spaces of the crystal lattice; an example of such a polymer is:

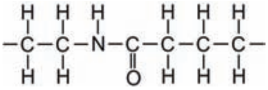


$$\left[\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & \mathrm{OH} & \end{array}\right]_n$$

polyvinyl alcohol (PVAL)

The OH group is small enough with respect to hydrogen to allow crystallization in a crystal lattice similar to polyethylene, albeit with some distortions. On the other hand, for example, atactic PVC is unable to crystallize because the Cl atom is much larger than the H atom.

iii. There is one side group attached to the chain that, however, can rotate freely around the chain; examples are the polyamides (nylons):

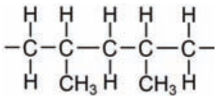


$$\begin{array}{ccccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{N} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & & & \| & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{H} & & & & \mathrm{O} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

nylon-6 (PA-6)

Here the oxygen atom can rotate freely. In the crystal all O atoms of a particular chain will be oriented in one plane, in this way they do not disturb the packing with neighbouring chains.

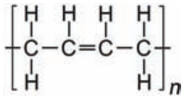
iv. The side groups are placed regularly, stereospecific. An example is given by:



$$-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-$$

isotactic polypropylene (PP)

v. The polymer consists of unsaturated main chains, and they are chiefly present in one configuration, cis or trans:



$$\left[-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

cis-1,4-polybutadiene (BR)

For all these examples it should be noted that not all polymers that *can* crystallize actually *will* crystallize, for instance the crystallization *rate* can be too low.

For crystallization the polymer chains must assume an ordered configuration, they must align in a parallel way. In practice the chains are not fully stretched, but they fold back and forth on themselves in a more or less regular way. These folded chains are packed together in a lamellar, plate-like structure with the folds occurring at the surfaces (see Figure 3.42).

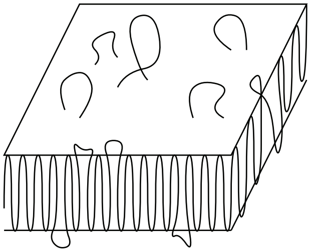


Figure 3.42. Lamellar polymer crystal.

Manipulation of these lamellae, for instance by stretching, may lead to fibrous structures where the polymer chains are fully stretched and lie parallel. These fibres have a very high tensile strength and modulus, like the PE fibre Dyneema®, developed by DSM (The Netherlands).

Since polymers consist of flexible chains of different length, which moreover, can have 'defects' like branches, the crystallinity never reaches 100%. Crystalline plastics are therefore *semicrystalline*, in-between the crystallites amorphous material remains present. One of the oldest models for a semicrystalline polymer is the fringed-micelle structure where the crystalline parts are embedded in an amorphous phase as shown in Figure 3.43. Some chain molecules, the tie molecules, act as connecting links between the different crystalline regions.

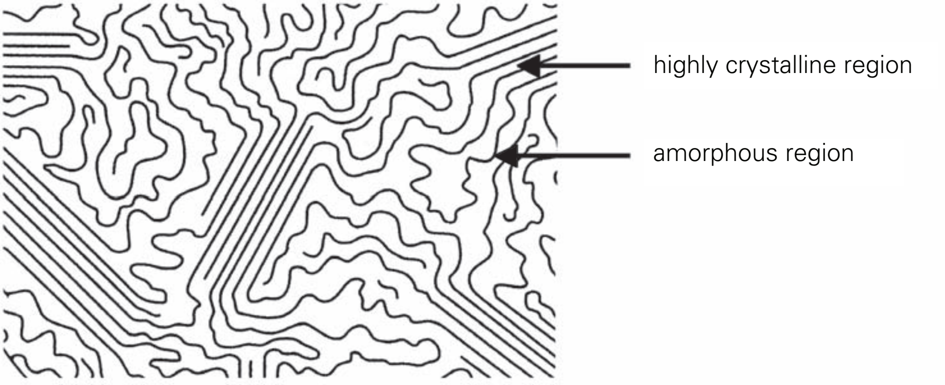


Figure 3.43. Fringed-micelle structure.

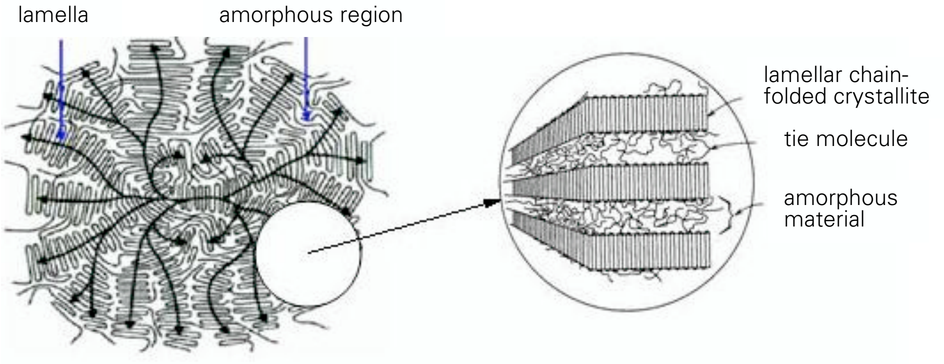


Figure 3.44. Spherulite.

Most polymers that are crystallized from the melt form *spherulites* (see Figure 3.44). Spherulites, as implied by the name, are spherical aggregates of crystallites grown from a primary nucleus. Within the spherulites also amorphous regions are embedded. The dimensions of the spherulites are in the order of 1 to 5 μm.

In practice the behaviour of semicrystalline polymers is distinctly different from that of purely amorphous polymers. Like before, the E-modulus as a function of temperature (see Figure 3.45) is very suitable to illustrate the (mechanical) behaviour. If a polymer would be 100% crystalline, then curve *a* would be followed: no glass-rubber transition, but a sharp decrease at T_m, the melting temperature of the polymer crystals. Curve *b* applies to an ideal semicrystalline polymer. However, this behaviour will never be found in practice, since the structure in the crystalline regions will not always be perfect. The result of imperfection is a statistical distribution of melting points, the upper limit being the melting point of a perfect polymer crystal and the lower limit being that of the most imperfect crystal. The distribution of melting temperatures causes the E-modulus to decrease gradually in the region between the glass transition and the melting point: curve *c*. In most cases the polymer turns into a viscous liquid on melting. For very high-molecular weights T_v can exceed T_m, and then part of the rubbery region will be preserved upon melting, as demonstrated in Figure 3.46.

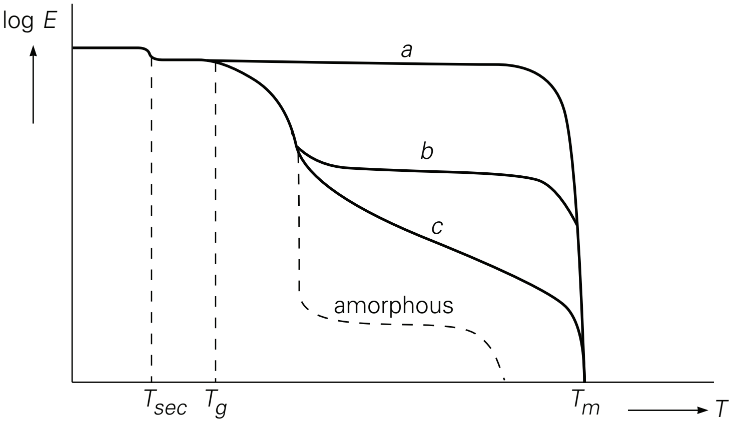


Figure 3.45. Log E as a function of temperature for a semicrystalline polymer.

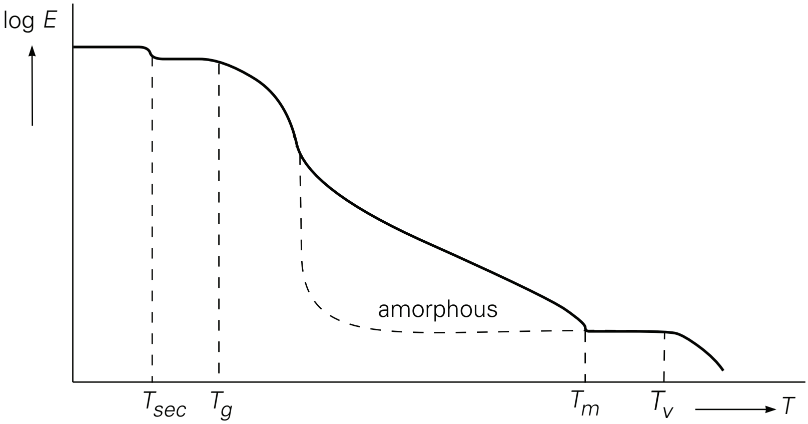
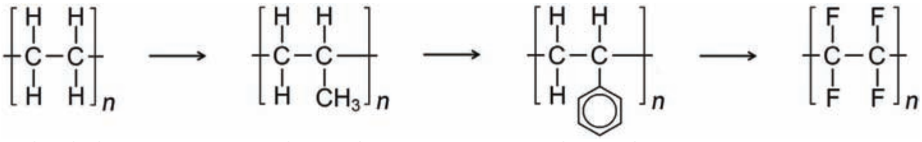


Figure 3.46. Log E as a function of temperature for a semicrystalline high-molecular weight polymer.

The melting temperature of a polymer is always higher than its glass transition temperature, the difference is usually around 200°C. For some polymers, such as PE, POM and PP, T_g lies below room temperature. This means that for this type of polymers room temperature lies between T_g and T_m in Figure 3.45 and Figure 3.46. In this case the E-modulus at room temperature is lower than that of glassy polymers, but higher than that of rubbers. As a result these thermoplastics feel 'leathery', they are supple but not rubbery.

The factors that determine the glass-rubber transition temperature also determine the position of the melting point. The influence of the flexibility of the polymer chains is expressed in the following series:



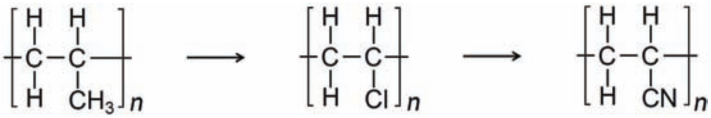
polyethylene T_m = 135°C

isotactic polypropylene T_m = 170°C

isotactic polystyrene T_m = 240°C

polytetrafluoroethylene T_m = 325°C

The influence of chain interactions is demonstrated in the sequence:



isotactic polypropylene T_m = 170°C

syndiotactic polyvinyl chloride T_m = 280°C

polyacrylonitrile T_m = 280°C

Since for understanding the behaviour of polymers in practice the transition temperatures are of utmost importance, at the end of this section a summary is given of all transitions occurring in polymers, in Table 3.12.

Table 3.12. Description of the various transition temperatures in plastics.

	type of transition	*phases involved*	*comment*
T_{sec}	secondary transition	glass-glass or crystalline-crystalline	only minor decrease of E, but of great importance for brittle or tough behaviour
T_g	glass-rubber transition or glass transition	glass-rubber	sharp decrease of E (in the order of a factor 1000) for an amorphous polymer, gradual decline for a semicrystalline polymer
T_v	flow temperature	rubber-liquid	always present in amorphous polymers, can also be found in crystalline polymers with large molecular weight
T_m	melting temperature	crystalline-liquid	only present in semicrystalline polymers

3.5.5 Liquid crystal polymers

Melting normally implies a complete loss of order of the polymer molecules. However, for some polymers the stiffness (see Section 3.5.3) of the chain molecules causes a certain degree of orientational and positional order to remain in the molten state. In general such phases are called liquid crystals and polymers that show this behaviour are called liquid crystal polymers or LCPs. As liquid crystal phases occur in-between the (solid) crystal and the isotropic (unordered) melt they are also called *mesophases* (*meso* = between) and the (side) groups causing the rigidity of the polymer molecules are the *mesogenic* groups.

Liquid crystalline behaviour can occur due to the presence of rigid mesogenic groups in the polymer backbone, *main chain LCPs*, and with mesogenic side groups attached to a flexible polymer backbone, *side chain LCPs*, see Figure 3.47. Also, liquid crystal (= LC) polymer networks are possible if the polymer backbone is cross-linked, or indeed bifunctional mesogenic side groups can form part of the network itself.

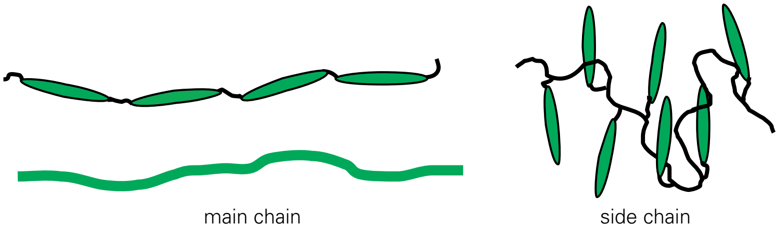


Figure 3.47. Main chain and side chain LCPs.

So far, we have discussed polymers that show liquid crystallinity in the melt. These polymers are called *thermotropic* liquid crystals. Often main chain LCPs cannot be processed from the melt due to the high melting point which is caused by the high stiffness of the polymer backbone. Alternatively, such polymers can often be processed from a liquid crystalline solution by dissolving the polymer in a strong acid. Polymers that show liquid crystallinity in solution are called *lyotropic* liquid crystals. In such cases often the phase behaviour can be represented in a phase diagram showing the various phases as a function of polymer concentration and temperature. If the temperature has a major effect on the phase behaviour the system can be considered as showing both thermotropic and lyotropic behaviour. Figure 3.48 shows a scheme for the classification of the various types of LC behaviour.

A variety of different LC phases are known and they differ in the way the mesogenic groups are organized. The differences in positional and orientational order are of great importance for the processing and application of the

LCPs involved. Figure 3.49 shows the most important types of arrangement of the mesogenic groups called *smectic, nematic* and *isotropic*, respectively.

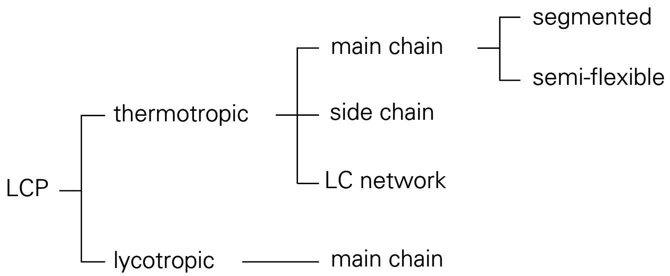


Figure 3.48. Simplified scheme for the classification of LCPs.

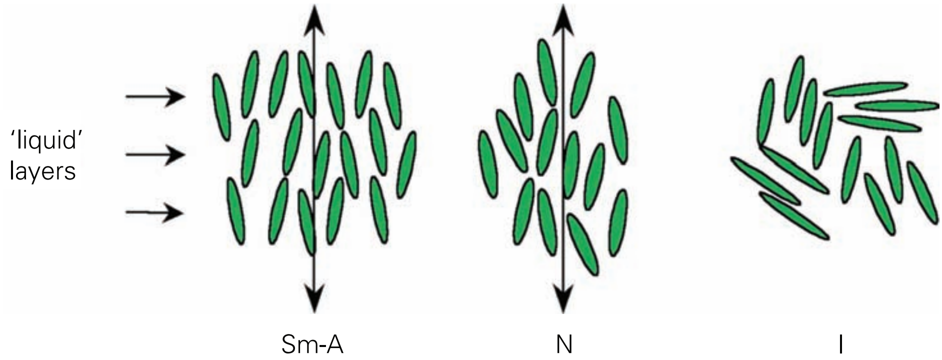


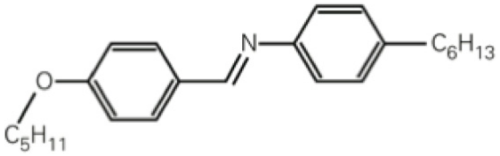
Figure 3.49. Smectic-A (Sm-A), nematic (N) and isotropic (I) phases.

The isotropic phase corresponds to the normal melt *i.e.* without positional or orientational order. The nematic phase has orientational order of the mesogens but no positional order, it is therefore an oriented liquid. Finally, in the smectic phases the mesogenic groups form layered structures, essentially a 1-dimensional crystal, while the layers remain liquid-like. In Figure 3.49 we show the simplest smectic phase, called smectic-A, although many more smectic liquid crystal structures are known, *e.g.* by tilting of the molecules in the smectic layers. The different smectic phases can be denoted as smectic-A, smectic-B and so on. It should be clear form the above that the nematic and smectic liquid crystal phases are structures with characteristics in-between those of a true crystal, which has both orientational and positional order, and the normal isotropic melt, which has neither. Also it is noted that similar to crystalline materials liquid crystal phases can have domain structures and defects which depend on the processing conditions, external fields, and applied boundary conditions.

Concerning the effect of the molecular structure on the formation of the various LC phases it will be clear that the prime aspect is the rigid shape of the mesogenic groups, or the rigidity of the polymer backbone itself in the case of the semi-flexible main chain LCPs. The types of chemical structures that give rise to this rigidity can be found by inspecting the examples listed in Table 3.13. In the case of semi-flexible main chain LCPs the nematic phase will generally be found, but not any smectic phases. It is important to realize that the formation of smectic phases with a layered structure is caused by the tendency for phase separation between the rigid and the flexible parts of the molecule. For this reason the tendency for formation of smectic phases will increase with increasing length of the flexible spacers, between the mesogens and the polymer backbone, or between the mesogens in the segmented main chain LCPs.

So far we have neglected the effect of temperature on the different structures. For instance on cooling down from a temperature where the liquid crystalline material is isotropic, nematic and smectic structures can be formed. The temperatures of transition are often denoted as: K T_{KA} Sm-A T_{AN} N T_{NI} I, where K is the shorthand notation for a crystalline phase, Sm-A for a smectic-A phase, N for nematic, and I for the isotropic phase. In this example T_{KA} is the melting point from the crystal phase to the smectic-A liquid crystal, and similarly for the other transitions.

As an example Figure 3.50 shows the structure and temperatures of transition of a low-molecular weight liquid crystal. It should be noted that the LCP transition temperatures are usually given in centigrades.

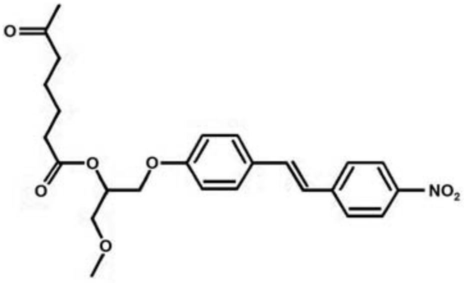
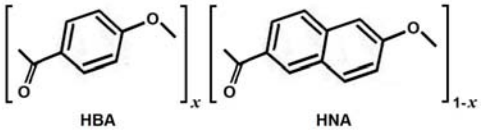
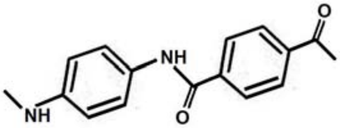
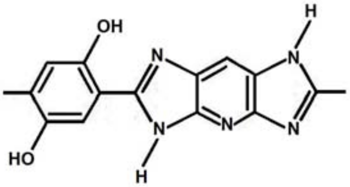
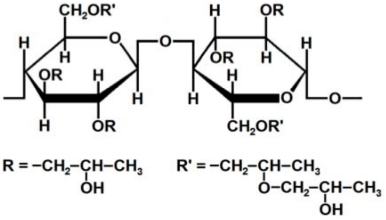


K 36 G 38.4 F 42.4 Sm-B 50 Sm-C 51.8 Sm-A 60.3 N 72.8 I

Figure 3.50. Chemical structure and LC phases of pentoxybenzylidenehexylaniline (phases G and F are partially disordered crystals).

In polymers that show thermotropic behaviour crystallization can be strongly suppressed. Instead of forming a fully amorphous glassy state, liquid crystal polymers will show vitrified liquid crystal structures below the glass transition. If for instance a nematic polymer melt is cooled through the glass transition a nematic glass (G_N) will result. Similar situations may occur with the other LC phases.

Table 3.13. Some examples of liquid crystal polymers.

type, name and phase behaviour	*structure*	*applications*
Thermotropic side chain LCP: *hydroxy-nitrostilbene* polyester, G_N 51 N 83 I		Has applications in data storage and optical devices
Thermotropic main chain LCP: *Vectra®: random copolyester of hydroxybenzoic and hydroxynaphtoic acid* forms a nematic melt at about 250°C		Is used as an engineerig polymer
Lyotropic main chain LCP: *poly(p-phenylene terephtalamide), PPTA* forms a nematic phase in H_2SO_4 between 8 and 20 wt% polymer concentration		Applied as a high performance aramid fibre, Kevlar® and Twaron®
Lyotropic main chain LCP: *M5* or *PIPD* forms a nematic phase in polyphosphoric acid		Experimental high performance fibre with enhanced properties
Lyotropic main chain LCP: *hydroxypropyl-cellulose, HCP* forms a nematic phase in water above 55 wt% polymer concentration		Mainly used as a water soluble polymer to modify viscosity. May be useful as a natural engineering plastic

Concerning the transition temperatures in the thermotropic polymers, these can be controlled by the chain stiffness (increases the transition temperatures) and the regularity of the chain. For example, the homopolymer of hydroybenzoic acid is found to be intractable and decomposes before melting, whereas the random copolymer of hydroybenzoic and hydroxynaphtoic acid (see Table 3.13) can be processed as a nematic melt, admittedly at a rather elevated temperature, and is an important engineering polymer for manufacturing high-temperature resistant precision components *e.g.* for the electronics industry. Similarly, the glass transition temperature of a side chain LCP will mainly be governed by the glass transition of the flexible polymer backbone, although the actual values will generally be higher than for the unsubstituted chains. In the case of side chain LCPs therefore the liquid crystal transitions and the location of T_g can to some extent be varied independently, respectively by modification of the backbone, the mesogenic group and the spacers. This makes them particularly important as functional polymers in optical applications where the molecular configurations have to be carefully designed to achieve the desired structure and properties. Applications of such materials are found in optical components for displays, and in various data storage devices.

Problem 3.10 *In view of the above, what is the key question to consider when processing an LCP?*