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Preface

This document, in accordance with the official LMD (Licence-Master-Doctorate) system programs, is an educational resource intended for first-year master's students in the Physics of Materials.

The document is divided into seven chapters:

The first chapter introduces the fundamental concepts of materials used in various industrial and research fields. It provides an overview of the importance of materials in technological advancements and manufacturing.

The second chapter offers a systematic classification of materials based on their chemical composition and physical properties, which are categorized into metals, ceramics, polymers, and composites.

The third chapter focuses on metals, starting with their crystalline structures. Metallic radii, metallic alloys in solution, and metallic glasses are discussed in detail. The key properties of metals, such as their electrical and thermal conductivity, are also explored, highlighting their significance in modern industry and technology.

The fourth chapter explores ceramics, concentrating on their specific bonds and structures. Silicate and non-silicate ceramics are examined, along with the methods of ceramic fabrication. The main properties of ceramics, such as hardness, heat resistance, and corrosion resistance, and their applications in various sectors are also discussed.

Glasses are examined in the fifth chapter, with a particular focus on the bonds and structures of silicate glasses. The deformation of glasses, reinforced glasses, and ceramic glasses are also covered. The manufacturing processes and applications of different types of glasses, as well as their specific properties, are analyzed to illustrate their wide-ranging use.

The sixth chapter focuses on polymers, describing the chemical structures of some common polymers and their microstructures. The methods of polymer fabrication, elastomers, and the main properties of polymers are examined. The applications of polymers are also discussed.

Composite materials are explored in the seventh chapter, focusing on fiber-reinforced plastics, metal matrix composites, and ceramic matrix composites. The specific properties and applications of composites, such as cement and concrete, are analyzed. The advantages of composite materials, such as their increased strength and light weight, are highlighted.

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Chapter VI: Polymers

Chapter VII: Composite materials

Chapter I: Materials science

I.1   Materials science:

Traditionally, materials have been categorized into three principal groups: metals, ceramics, and polymers. Metallic materials encompass pure metals like titanium, iron, or copper, as well as a wide array of alloys, including historically significant materials like bronze, brass, and steel. Ceramics bring to mind materials like porcelain, silicon carbide, glass, and synthetic gemstones such as ruby and zirconia. Polymers consist mainly of carbon compounds and include well-known materials like poly (vinyl chloride), polyethylene, and nylon, as well as important biological molecules such as DNA.

In addition to these principal divisions, two other categories deserve mention: composites and biomaterials. Composites are combinations of materials sourced from more than one of the aforementioned groups and exhibit superior properties compared to their individual components. For instance, glass-fiber (ceramic) reinforced epoxy resin (polymer) displays mechanical properties that surpass those of the individual constituents. One of the most notable composites is concrete, which consists of cement and aggregate, a stony material.

Biomaterials are naturally occurring materials with significant properties, such as wood, silk, and bone, and they are often composite in nature. Due to the exceptional properties of many biomaterials, considerable efforts are made to synthetically replicate these materials through biomimetics.

At first glance, metals, ceramics, and polymers may appear to have little in common, primarily due to two key factors: the chemical bonding that holds their atoms together and the microstructures inherent in each material. These differences are readily apparent in typical examples of each material. However, this disparity is deceptive. Consider ceramic superconductors, for instance; many ceramics can be categorized as metals in certain contexts. Similarly, some polymers exhibit electronic conductivity surpassing that of metals and find applications in lightweight batteries and electronic devices.

Chapter II: Materials classification

II.1. Materials classification

II.1.1. Definition

The composition of the world around us is comprised of tiny discrete particles, each with a sub-microscopic size. These particles' behaviour is governed by atomic theories, and the arrangement of materials can vary greatly, from the chaotic disarray of atoms or molecules in a low-pressure gas to the nearly perfect order found in monocrystals.

In this introductory text, materials are defined as solid substances that humans use to create the foundations of their living environments. In fact, no object can exist without materials. Every facet of human activity relies on materials, whether it's the production of integrated circuits or the construction of hydroelectric dams. They even play a role in our bodies, reinforcing or replacing damaged biomaterials. Materials are as essential to our society as food, energy, and information, yet their fundamental importance is often overlooked.

It's important to note that this introductory text exclusively focuses on solid materials and excludes liquids, gases, and solid combustibles.

II.2. The three classes of materials:

Materials are categorized based on various criteria, including their composition, structure, and properties. In this context, we can distinguish three major groups of materials (see Figure II.1). This categorization relies on the atomic structures and the types of bonds present:

- Metals and their alloys (characterized by metallic bonding).

- Organic polymers (held together by covalent bonding and secondary bonding).

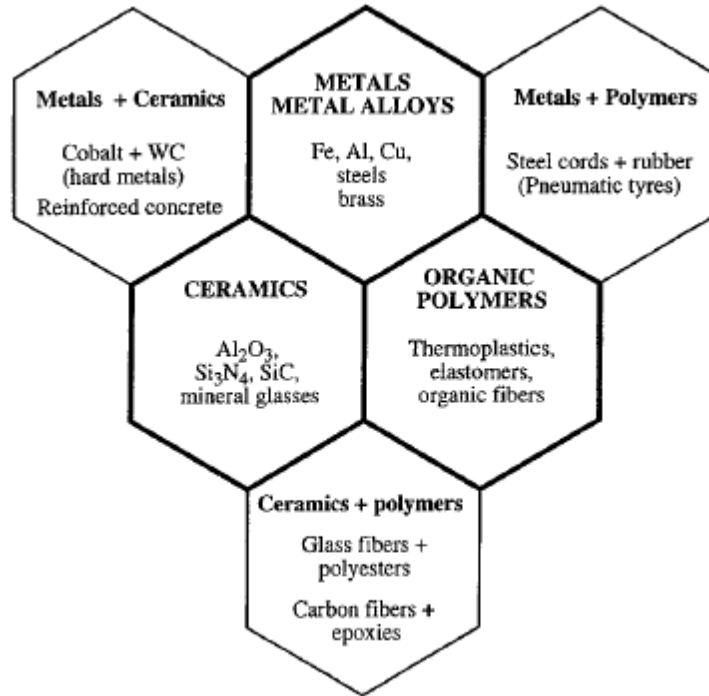- Ceramics (exhibiting ionic bonding and covalent bonding).

Figure II.1: The three classes of materials: metals, ceramics ad organic polymers with some possible combinations of composite materials.

This classification can be elucidated by referring to the Periodic Table of the Elements (Mendeleev's Table, as shown in Figure II.2).

   The majority of elements fall into the category of metals, constituting approximately 70% of the elements, mainly located on the left and center of Mendeleev's table. On the other hand, non-metals like oxygen are situated on the right-hand side of the Periodic Table. In the intermediate region between metals and non-metals, there are specific elements such as carbon and silicon (semiconductors) that do not fit neatly into this straightforward classification. At room temperature, the majority of metals exist as monoatomic solids. Iron, aluminium, and copper are among the most commonly utilized metals. Metallic alloys are typically composed of two or more metals, like brass (a combination of copper and zinc), but they can also incorporate non-metallic elements. Most of steels, for instance, fall into this category as alloys of iron and carbon. Metals and their alloys are typically conductors of heat and electricity, and they are

opaque to visible light, reflecting it. They are generally hard, rigid, and capable of undergoing plastic deformation. Additionally, a significant number of metals have high melting points (Tm).

Organic polymers are materials composed of molecules that form lengthy chains of carbon atoms, often attached to elements like hydrogen or chlorine, or groups of atoms such as the methyl radical (-CH3). Other elements like sulfur, nitrogen, and silicon can also be part of the chain composition. Well-known organic polymers include poly (vinyl chloride) (PVC), polyethylene (PE), and polystyrene (PS). They are frequently known by their trade names, such as polymethylmethacrylate (PMMA or 'Plexiglas®'), polyamides (PA: 'Nylons®'), and polytetrafluoroethylene (PTFE or 'Teflon®'). Organic polymers, including organic glasses and rubbers, exhibit a wide range of physical properties. They are typically insulators of electricity and heat, lightweight, and easily formable. Unlike metals, non-oriented polymers lack rigidity and generally cannot withstand temperatures exceeding 200°C.

Ceramics are inorganic materials that are typically formed by combining a limited number of metallic elements (e.g., Mg, Al, Ti) with non-metallic elements, primarily oxygen. Initially, the term "ceramic" referred to oxides like silica (SiO_2) and alumina (Al_2O_3), but it has since been expanded to include other atomic combinations such as tungsten carbide (WC) or silicon nitride (Si_3N_4). Ceramic materials are renowned for their resistance to high temperatures and mechanical stress, making them fireproof. However, ceramics have a broader range of applications beyond this. They are generally very hard and serve as abrasives. Most ceramics are insulators of electricity and heat, although some are excellent thermal conductors, such as diamonds. Many ceramics find important uses in electrical equipment and electronics. Mineral glasses, composed of oxide combinations (SiO_2 + Na_2O + CaO, etc.) in an amorphous structure, also fall under the category of ceramics. Typically, both glass and ceramics are brittle materials unsuitable for applications where mechanical and thermal shocks are significant.

The fusion of three distinct material categories can yield composite materials, as illustrated in Figure II.1. Composite materials are composed of two or more dissimilar materials that synergistically leverage their unique properties. An example of this synergy can be seen in epoxy resins (a type of polymer) reinforced with glass fibers, resulting in lightweight composites possessing exceptional mechanical strength. Another instance of a composite material is found in concrete, which is a blend of cement and gravel.
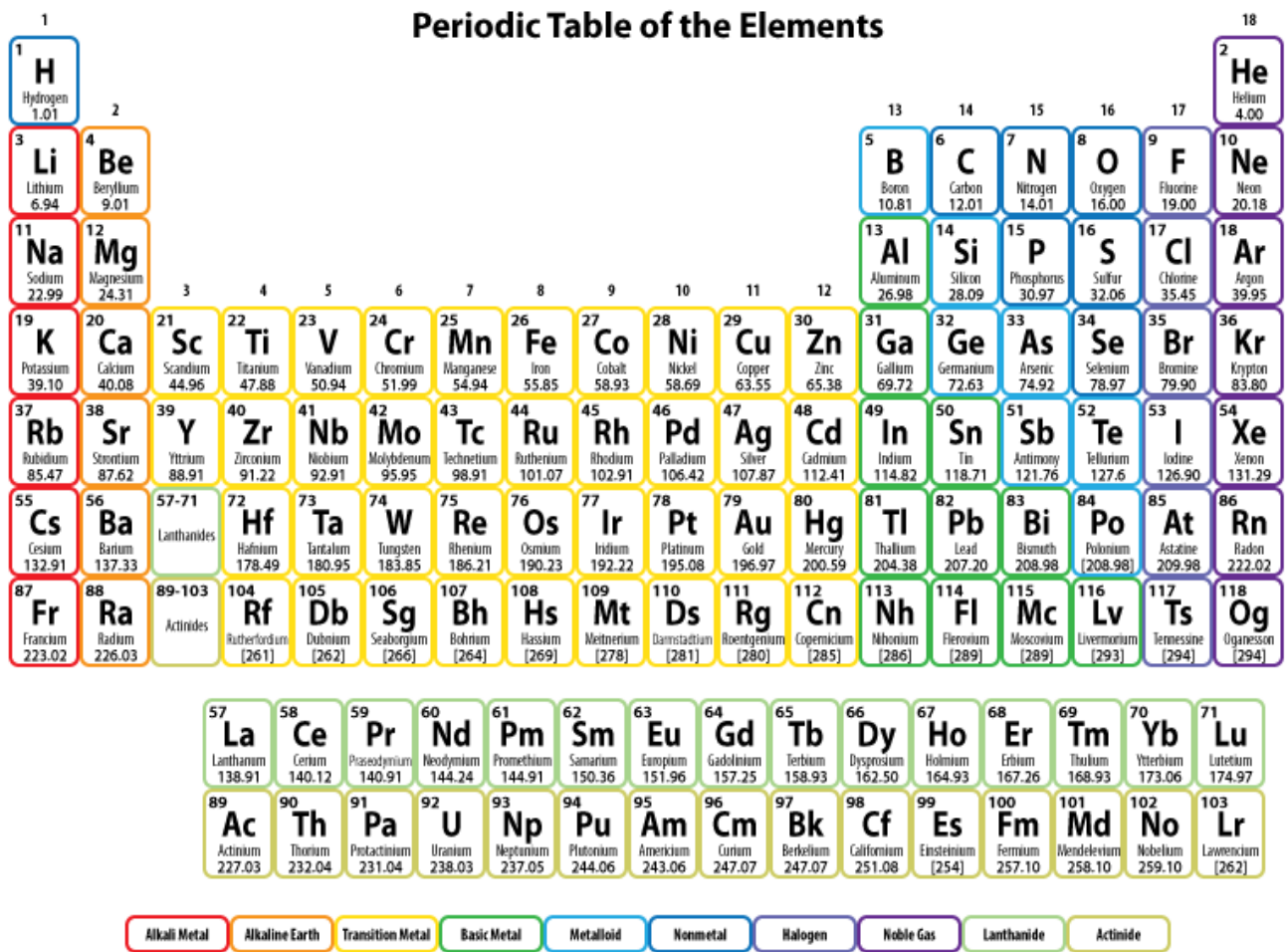

Figure II.2: Periodic table of elements.

The categorization of materials into three primary classes, primarily determined by atomic and structural attributes, offers convenience but lacks a rigid foundation. For example, consider diamond, which can be viewed as a three-

dimensional polymer due to its composition of carbon atoms. Despite this, its exceptional hardness and mechanical characteristics align it more closely with ceramics. Furthermore, electrical conductivity is no longer exclusive to metals, as certain oxides (such as VO_2 and $YBa_2Cu_3O_7$) and some organic materials also exhibit electrical conductivity.

It's important to recognize that any classification of materials possesses an inherent degree of arbitrariness, as there are no clear-cut boundaries between these three material classes. Alternative classifications based on specific material properties, such as semi-conductivity, can also be justified.

Exercise:

1. Based on which criteria materials were being categorized?
2. How to get ceramics?
3. What is the crystal structure of: metals, polymers, and ceramics?
4. How composite materials are composed?

Chapter III : Metals

III.1.   Metals

In broad terms, approximately 75% of elements can be categorized as metallic. Given the diversity in outer electron configurations resulting from this, one might anticipate the emergence of a wide array of metallic structures, and these variations would follow a predictable pattern across the periodic table.

However, it is rather astonishing to discover that the majority of metallic elements adopt just three distinct structures. This phenomenon occurs because the outer electrons of metals are dispersed throughout the crystal lattice, leaving behind a nearly spherical core. As a result, the crystal structures of many metals can be reasonably approximated as sphere packings. In contrast, alloys, which consist of two or more metallic elements, lose this simplicity and exhibit a far greater range of structures.

III.2.   Pure metals' crystal structures:

Most pure metals tend to adopt one of three primary crystal structures: A1, also known as the copper structure and characterized by cubic close-packing; A2, referred to as the tungsten structure, featuring a body-centered cubic arrangement; or A3, the magnesium structure, which exhibits hexagonal close-packing (as shown in Figure III.1). The differences in energy between these structures are relatively small, and variations often occur due to changes in temperature and pressure. These distinct structural forms are commonly referred to as allotropes, as summarized in Table III.1.

Interestingly, considering the numerous structural possibilities that arise from hexagonal (ABAB) or cubic (ABCABC) close-packing, it is somewhat surprising that only a few complex arrangements are observed. Cobalt is a notable exception to this trend. Below approximately 435°C, cobalt's structure consists of a disordered, random stacking of A, B, and C planes of metal atoms. Careful annealing at lower temperatures can transform it into the A3 structure, which, in turn, transitions to the A1 structure when heated above 435°C. Lanthanum, praseodymium, and neodymium adopt a mixed close-packing

arrangement with an ABAC repeat, while samarium's packing repeat follows the pattern BABCAC.

As depicted on the right-hand side of Figure III.1, more complex structures emerge for certain elements that were previously categorized as semi-metals. In these elements, the outer electrons do not fully integrate into the structure, and the shapes of electron orbitals start influencing bonding. This effect becomes noticeable in the case of mercury, often described as the anomalous metal, where the structure can be conceptualized as a compressed A1 structure along one body diagonal, resulting in a rhombohedral structure. Similarly, indium exhibits a slightly distorted A1 structure.

Greater bonding effects are observed within the carbon group. At standard temperature and pressure, carbon (in the form of graphite) exhibits a mixture of sp^2 and weaker van der Waals bonding. Under high pressure, graphite transforms into the diamond structure, where atoms are connected by sp3-hybrid bonds arranged tetrahedrally. Silicon and germanium both adopt the diamond structure under normal conditions. Tin's bonding behaviour lies on the borderline, with a-tin (grey tin) being the stable allotrope at temperatures below 13.2°C. Grey tin features the diamond structure with sp3-hybrid bonding. At temperatures above 13.2°C, b-tin (white tin) becomes stable, representing the metallic form of tin. The transition from white to grey tin is gradual, and metallic impurities stabilize the metallic form, making it the predominant state of tin. Despite being metallic, the structure of white tin is complex and does not conform to the A1, A2, or A3 structures, highlighting the significance of bonding effects. For lead, the increased atomic size leads to extensive delocalization of outer electrons, resulting in a metallic solid with an A1-type structure.

In the semimetals antimony, arsenic, and bismuth, bonding effects are more pronounced, and their structures deviate significantly from the typical metal structures. Among these, bismuth, the heaviest element, displays the most metallic properties, while phosphorus, positioned above antimony in the periodic table, is not even considered a semimetal.

Li A2 0.3509	Be A3 a 0.2286 c 0.3585												B	C
Na A2 0.4291	Mg A3 a 0.3209 c 0.5211												Al A1 0.4050	Si
K A2 0.5321	Ca A1 0.5588	Sc A3 a 0.3309 c 0.5268	Ti A3 a 0.2951 c 0.4686	V A2 0.3024	Cr A2 0.2885	Mn	Fe A2 0.2867	Co	Ni A1 0.3524	Cu A1 0.3615	Zn A3 a 0.2665 c 0.4947	Ga	Ge	
Rb A2 0.5705	Sr A1 0.6084	Y A3 a 0.3648 c 0.5732	Zr A3 a 0.3232 c 0.5148	Nb A2 0.3300	Mo A2 0.3147	Tc A3 a 0.2738 c 0.4393	Ru A3 a 0.2706 c 0.4282	Rh A1 0.3803	Pd A1 0.3890	Ag A1 0.4086	Cd A3 a 0.2979 c 0.5620	In	Sn	
Cs A2 0.6141	Ba A2 0.5023	La	Hf A3 a 0.3195 c 0.5051	Ta A2 0.3303	W A2 0.3165	Re A3 a 0.2761 c 0.4458	Os A3 a 0.2734 c 0.4392	Ir A1 0.3839	Pt A1 0.3924	Au A1 0.4078	Hg	Tl A3 a 0.3457 c 0.5525	Pb A1 0.4950	

Figure III.1: The crystal structures of the metallic elements at room temperature (25 C°) and atmospheric pressure. Unit cell parameters (a for cubic structures) are in nm. A1: copper (cubic close-packed). A2: tungsten (body-centred cubic). A3: magnesium (hexagonal close-packed).

Table III.1: Allotropic structures of some metals.

Element	Room temperature structure	High-temperature structure	Transition temperature/°C
Calcium, Ca	A1	A2	445
Strontium, Sr	A1	A2	527
Scandium, Sc	A3	A2	1337
Titanium, Ti	A3	A2	883
Zirconium, Zr	A3	A2	868
Hafnium. Hf	A3	A2	1742
Ytterbium, Yb	A3	A2	1481
Iron, Fe	A2	A1	912
Cobalt, Co	(A3)	A1	435

III.3.   Metallic radii:

Assuming that metallic structures consist of touching spherical atoms, it becomes relatively straightforward to calculate metallic radii when armed with the unit cell's size (refer to Figure III.2). Below, you'll find the correlation between the cell edge (a for cubic crystals, a and c for hexagonal crystals) and the radius of the constituent atoms (r) for the three prevalent metallic structures.

A1, copper structure, face-centered cubic: The atoms touch each other along the diagonal of a cube face, resulting in the following relationship:

$$r = a/2\sqrt{2} = a/\sqrt{8}$$

The separation of the close-packed (111) atom planes, (along a body diagonal of the cube) is:

$$a/\sqrt{3} = \sqrt{8}r/\sqrt{3} \approx 1.633r$$

Each atom has 12 nearest neighbours.

A2, tungsten structure, body-centered cubic: The atoms are in contact along a cube's body diagonal, which is equivalent to 4r. This distance is also equal to [insert equivalent expression], resulting in the following relationship:

$$r = \sqrt{3}a/4$$

Each atom has 8 nearest neighbours.

A3, magnesium structure, hexagonal close-packed: The atoms touch along the a-axis, leading to the following relationship:

$$r = a/2$$

The distance between the closely packed atomic planes is c/2. In an ideal close-packed structure, the ratio of c/a is: $\sqrt{8}/\sqrt{3} = 1.633$

Each atom has 12 nearest neighbours.

Li	Be											B	C
0.1562	0.1128												
Na	Mg											Al	Si
0.1911	0.1602											0.1432	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
0.2376	0.1974	0.1641	0.1462	0.1346	0.1282	0.1264	0.1274	0.1252	0.1246	0.1278	0.1349	0.1411	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
0.2546	0.2151	0.1801	0.1602	0.1468	0.1400	0.1360	0.1339	0.1345	0.1376	0.1445	0.1568	0.1663	0.1545
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
0.2731	0.2243	0.1877	0.1580	0.1467	0.1408	0.1375	0.1353	0.1357	0.1387	0.1442		0.1716	0.1750

Figure III.2: Metallic radii, nm, for 12-coordinated elements.

Similar to ionic radii, the experimentally determined atomic radius is observed to be influenced by the number of closest neighbouring atoms, known as the coordination number (CN) of the atom under consideration. In both the A1 and A3 structures, atoms are surrounded by 12 nearest neighbours (CN 12), and the derived radius is suitable for this level of coordination. Conversely, in the A2 structure, atoms are surrounded by eight closest neighbours (CN 8). To ensure a consistent set of values, it becomes necessary to convert the radii measured in relation to this structure into values suitable for 12-coordination. This conversion can be achieved using the empirical formula:

$Radius\ (CN\ 12) = 1.032\ r\ (CN\ 8) - 0.0006$; when the radii are measured in nm.

The metallic radii of several important elements, including Mn, Ga, and Sn, exhibit intricate structures that defy the application of the straightforward rules mentioned earlier. For these latter elements, their radii are determined by comparing interatomic distances in various alloys with appropriate structures.

Several noteworthy trends emerge from this analysis. In the case of the well-behaved alkali metals and alkaline earth metals, atomic radius increases smoothly with increasing atomic number. Similarly, within the d-transition metals, there is a general trend of increasing atomic radius as one moves down a period. This pattern also holds true for the lanthanoids and actinoids.

III.4.   Alloy solid solutions

Alloys hold significance due to their propensity for exhibiting superior mechanical properties when compared to the pure elements. Alloys encompasses a vast array of compositions, many of which show intricate and unconventional structures. Herein, we will focus on just two categories of alloys, both closely aligned with the structures of the pure metals.

Substitutional solid solutions have the structure of one of the constituent metals, known as the parent structure. In this type of alloy, the alloy-forming (or foreign) atoms simply take up positions within the structure that are typically occupied by the parent atoms. Conversely, interstitial solid solutions come into

being when very small foreign atoms infiltrate the parent structure and settle within the typically vacant interstitial positions. As their names suggest, in both of these examples, the foreign atoms are often perceived as being in a state of solution within the matrix of the parent metal.

III.4.1.   Substitutional solid solutions

The possibility of establishing a substitutional solid solution between two metals hinges on a range of chemical and physical attributes. Hume-Rothery delved into numerous alloy systems during the early 20th century, with the goal of unraveling the underlying principles governing alloy formation. His discoveries regarding the creation of substitutional solid solutions are encapsulated in the empirical Hume-Rothery solubility rules, which dictate the likelihood of achieving a solid solution. These rules are as follows:

1. The crystal structure of each element in the pair is identical.
2. The atomic sizes of the atoms should not vary by more than 15%.
3. The elements should not significantly differ in electronegativity, as such differences lead to compound formation. Hence, they should be positioned closely on the periodic table.
4. The elements must share the same valence, indicating they should belong to the same group on the periodic table.

Even though these guidelines were formulated a century ago, they remain valuable for modeling substitutional alloy formation. These rules, for instance, predict that copper-nickel and copper-gold should readily form extensive substitutional solid solutions. However, they do not foresee whether the atoms in the solid solution will arrange themselves in a specific order. In such instances, a new phase, termed an ordered solid solution, will form. This phenomenon occurs in many systems, particularly when random substitutional solid solutions are annealed, involving heating at lower temperatures for a specific duration.

For example, a copper-gold alloy, when subjected to high temperatures near its melting point (approximately 890°C) and then rapidly cooled, exhibits a random distribution of copper and gold atoms within the sites of the A1 (face-centered cubic) structure (Figure III.3 a). However, when the same material is annealed at around 400°C, it yields ordered phases known as Cu_3Au and CuAu.

The copper-rich alloy phase, Cu_3Au (Figure III.3 b), situates gold atoms at the corners of a cubic unit cell and copper atoms at the face centers. The ordered structure of the CuAu alloy (Figure III.3 c) consists of alternating (100) planes composed of either copper or gold atoms and is known as the CuAu I structure. More complex arrangements also arise; in the CuAu II structure (Figure III.3 d), a regular pattern of antiphase boundaries spaced every five CuAu unit cells results in an overall repetition along the c-axis, approximately ten times the cubic cell parameter.

These ordered structures formed through annealing are commonplace and significantly influence the physical, particularly mechanical, properties of substitutional alloys.
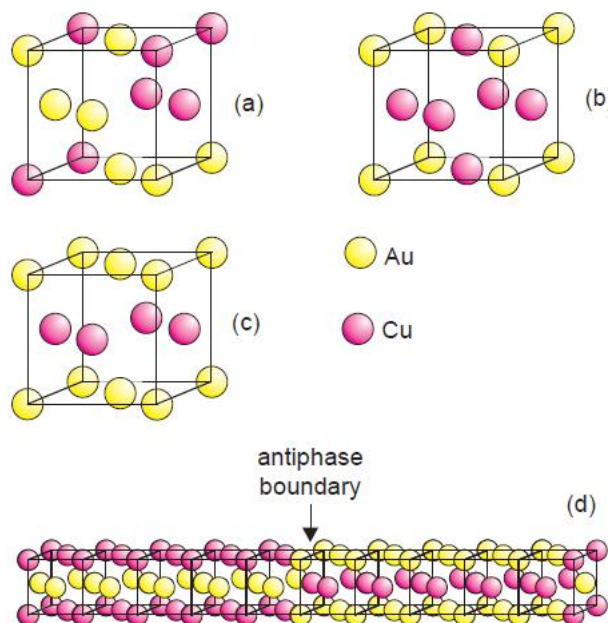

Figure III.3: The crystal structures of: (a) disordered CuAu; (b) ordered Cu3Au; (c) ordered CuAu I; (d) ordered CuAu II.

III.4.2. Interstitial solid solutions

In a manner analogous to the requirement for similar atomic sizes to create extensive substitutional solid solutions, the formation of an interstitial solid solution necessitates that the radius of the foreign atom be significantly less than half the atomic radius of the parent atoms. Traditionally, the most extensively examined interstitial alloys involve transition metals combined with carbon and nitrogen. The inclusion of these foreign atoms into the crystal structure significantly enhances the hardness of the metal. Globally, steel remains the most prominent traditional interstitial alloy, characterized by the random distribution of carbon atoms within interstitial sites within the face-centered cubic structure of iron, forming the austenite phase. More recently, the focus has shifted towards hydrogen storage, and interstitial alloys, which involve the incorporation of hydrogen into metals, have garnered substantial interest.

In interstitial alloys, foreign atoms can occupy sites with either tetrahedral or octahedral geometries. In both the A1 (face-centered cubic) and A3 (hexagonal) structures, there are twice as many tetrahedral sites as there are octahedral sites, and these sites are equivalent in number to the metal atoms. In the A1 structure unit cell, containing four metal atoms, the octahedral sites are positioned at the midpoints of each of the cell edges, with an additional site at the cell center. Each site on a cell edge is shared by four cells, and with 12 cell edges, there are $^{1}/_{4} \times 12$ sites at the edges plus one at the cell center, totaling four sites. The tetrahedral sites are distributed evenly throughout each quarter of the unit cell, resulting in eight tetrahedral sites. In the A3 structure, which contains two metal atoms per unit cell, there are four tetrahedral sites and two octahedral sites. In both structures, all the tetrahedral and octahedral sites share identical geometries.
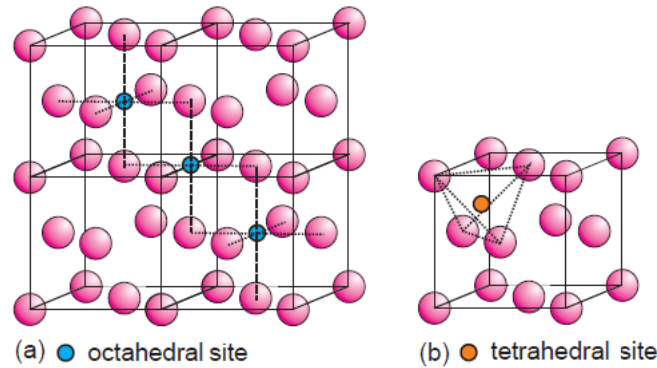
Figure III.4: (a) Octahedral and (b) tetrahedral sites in the A1 structure. Four-unit cells are drawn in (a). Not all equivalent sites are marked.

In the A2 structure (body-centered cubic), there are also 12 tetrahedral and 6 octahedral sites available. The octahedral sites are situated on all the cube faces, while the tetrahedral sites, also on the cube face, are slightly below the octahedral sites. Notably, the geometries of these tetrahedral and octahedral sites differ slightly from those in the A1 and A3 structures. Furthermore, various tetrahedral positions can be found in this structure.

In all three structures, the octahedral sites are larger and can accommodate both carbon and nitrogen atoms, while the smaller tetrahedral sites are primarily suitable for hydrogen occupancy.

The process by which interstitial alloys are formed exhibits similarities across all systems. A reactive gas, such as hydrogen for hydrides, methane for carbides, or ammonia for nitrides, decomposes on the metal surface. The resulting atoms can then enter the structure, occupying sites randomly. The resulting phases are often referred to as "alpha-phases." Continuous reactions can lead to the development of new structures, either through the ordered arrangement of impurity atoms, as seen in substitutional alloys, or through extensive structural rearrangements, as exemplified by cementite (Fe_3C).
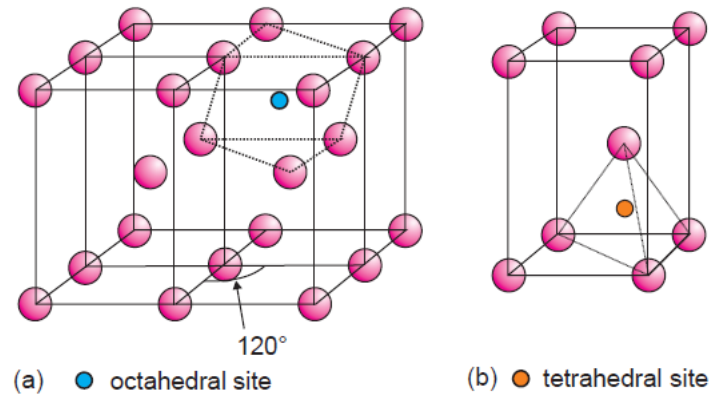
Figure III.5: (a) Octahedral and (b) tetrahedral sites in the A3 structure. Four-unit cells are drawn in (a). Not all equivalent sites are marked.

Beyond the size of the foreign atoms, the sites they occupy, and the degree of site occupancy depend critically on chemical interactions between the species. For instance, in the alpha-phase NbH_x, only a fraction of the tetrahedral sites with specific geometry are occupied. Furthermore, the limiting composition of the alpha-phase, approximately $NbH_{0.1}$, is achieved when only a portion of these particular sites is filled. At higher hydrogen concentrations, chemical interactions induce the formation of the hydride NbH.

Figure III.6: (a) Octahedral and (b) tetrahedral sites in the A2 structure. Two-unit cells are drawn. Not all equivalent sites are marked.
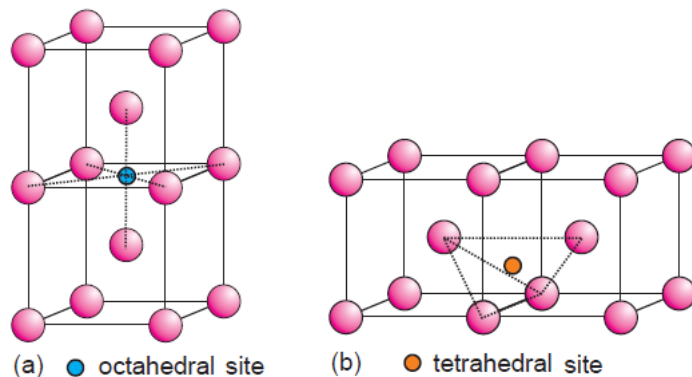
III.5.   Metallic glasses

To create metallic glass through supercooling, it is imperative to counteract the innate tendency of the liquid to crystallize. This can be accomplished through several approaches. Firstly, employing a system with a profound eutectic point is advantageous, as it allows the liquid to cool significantly before initiating

solidification. Secondly, utilizing a system composed of multiple metals, each of which crystallizes in distinct structures, hinders crystallization. Lastly, mixtures of atoms with significantly varying sizes resist crystallization. These considerations propose a general formula for metallic glasses, typically represented as $T_{70–90}(SM)_{0–15}(NM)_{10–30}$, where T denotes one or more transition metals, (SM) signifies one or more semimetals like Si or Ge, and (NM) represents one or more nonmetals such as P or C.

The earliest metallic glasses were produced by expelling a stream of liquid metal onto a rapidly rotating copper disc cooled with liquid nitrogen, achieving an extraordinary cooling rate of approximately $10^5–10^6 Ks^{-1}$. The first non-crystalline metallic material created using this method had the composition $Au_{75}Si_{25}$. Metallic glass ribbons were explored in the 1970s and 1980s for applications as soft magnetic transformer cores. A commonly used material for this purpose is METGLAS, with a composition of $Fe_{40}Ni_{40}P_{14}B_6$. Other examples of transformer core materials include $Fe_{86}B_8C_6$ and $FeB_{11}Si_9$.

By the end of the 1980s, research into more intricate systems allowed the fabrication of glassy metals at significantly slower cooling rates, down to $10 \ Ks^{-1}$. This breakthrough enabled the production of bulk metallic glasses using conventional casting methods. Bulk glasses possess unique chemical and physical properties that render them superior to polycrystalline alloys for various applications. Glasses with complex compositions like $Fe_{72}Al_5Ga_2P_{11}C_6B_4$ are employed as magnetic materials. Glass alloys renowned for their outstanding mechanical properties include the Vitreloy (or Vitralloy) family, with compositions closely resembling $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}B_{27.5}$, employed, among other things, in the manufacturing of golf club heads.

III.6.   The principal properties of metals

Metals have been distinguished throughout history by their shiny appearance and their unique ability to be shaped, bent, twisted, or beaten into thin foils without losing their formed shape. Beyond this, metals exhibit excellent electrical and thermal conductivity. When different metals are joined, they can form

thermocouples, generating a current when the two ends are at different temperatures. These properties are a result of the metallic bond, which arises from the interaction of bonding, crystal structure, and microstructure. In this bonding model, free electrons can move throughout the metal with minimal thermal or electrical force, as described by the Wiedemann-Franz law.

$$\frac{thermal\ conductivity}{electrical\ conductivity} = \frac{3Tk_B^2}{e^2}$$

The sheen of metals is also attributed to these free electrons. When light photons hit the metal surface, those near the Fermi surface can absorb the photons, and then they can return to their original energy levels, re-emitting the photons. Understanding a metal's reflectivity requires knowledge of the Fermi surface's exact shape and the density of energy levels at this surface.

When dissimilar metals are joined, electrons flow from the metal with a higher Fermi energy to the one with a lower energy level, giving rise to thermoelectric effects and the operation of thermocouples. The Fermi energy is also connected to a metal's susceptibility to corrosion.

The addition of other metals or non-metals in small amounts doesn't dramatically change these physical properties, but it generally hampers electron transport, leading to decreased electrical conductivity. The formation of new phases or alloys can cause abrupt changes in electrical conductivity.

One important mechanical property of metals is ductility, meaning they can be easily deformed without breaking and retain their deformed shape indefinitely. This property is attributed to the crystal structures of metals, with their spherical atoms allowing for easy deformation. Dislocations in crystals play a key role in allowing deformation to occur without breaking metallic bonds.

Metals can be hardened through various methods, such as pinning dislocations to prevent easy deformation. Impurities and the formation of substitutional or interstitial alloys can also contribute to hardening. Precipitates formed by

alloying and annealing further increase a metal's hardness. Steels, for instance, can be hardened through the incorporation of carbon or nitrogen and subsequent heat treatment. Metals that contain large quantities of precipitates can become brittle.

In summary, metals possess distinctive properties and can be modified to exhibit various mechanical and electrical characteristics. This section provides an overview of these properties and their origins.

Exercise:

1. What are the crystal structures of pure metals?
2. What does allotropes mean?
3. What are alloy solutions?
4. Why alloy solid solutions are important?
5. What are the types of alloy solid solutions?
6. How to get a substitutional solid solution?
7. What do parent and alloy-forming atoms mean?
8. How to get an interstitial solid alloy?
9. What are the rules to achieve a substitutional solid solution?
10. What does the formation of an interstitial solid solution necessitate?
11. What are metallic glasses?
12. How we can get metallic glasses?
13. What is the importance of metallic glasses?
14. How metals could be hardened?

Chapter IV : Ceramics

IV.1. Introduction

Ceramics are inorganic materials produced through high-temperature chemical processes. While most ceramics are comprised of oxides, the term encompasses various other inorganic substances, including silicides, nitrides, oxy-nitrides, hydrides, and more. Ceramics are typically characterized as chemically stable materials that possess hardness, brittleness, and serve as excellent thermal and electrical insulators. Nevertheless, noteworthy exceptions include ceramics capable of conducting electricity like metals.

It's practical to categorize ceramics based on their composition and intended usage. Traditional ceramics, primarily silicate-based, include items like bricks, drainage pipes, porcelain, and decorative ceramic pieces, mainly serving utility and aesthetic purposes. Engineering ceramics, on the other hand, stand out for their mechanical strength and are employed to broaden the operational capabilities of metallic components. They are prized for their resistance to high temperatures and extreme hardness, finding application in areas like protective coatings on metallic parts (e.g., titanium nitride, tungsten carbide, diamond), heat-resistant components (valves, cylinder liners, ceramic shields, and furnace linings), high-speed cutting tool inserts (transition metal carbides), and abrasive materials (such as alumina, silicon carbide, and diamond). Electro-ceramics represent a distinct category, characterized by their exceptional electronic properties, ranging from insulating to superconducting. They play a pivotal role in gas sensors, temperature sensors, batteries, fuel cells, and other electronic applications. Ceramic magnets are widely used in motors, and ceramics also find importance in fluorescent lighting and as integral components of computer displays.

IV.2. Bonding and structure of silicate ceramics

The crust Earth consists predominantly of silicates, which also make up the majority of semiprecious gemstones. Natural silicates, minerals that originated from complex molten magma, exhibit a variable composition, with each mineral

having an ideal composition if it were perfectly homogeneous. Isomorphous replacement is a common phenomenon in minerals, involving the substitution of some cations by others of similar size, even if their charges differ. Cations like Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} are readily interchangeable, as are anions like O^{2-}, F^-, and OH^-. Aluminum, located to the left of silicon on the periodic table, holds a unique position in silicate chemistry as it can randomly and to an indefinite extent replace silicon in silicates. Isomorphous replacement leads to substitutional defects in the crystal structure. To illustrate this, consider the mineral hornblende, with an ideal composition of $Ca_2Mg_2(Si_4O_{11})_2(OH)_2$. A typical analysis of a naturally occurring sample may reveal that nearly a quarter of the silicon is replaced by aluminum. Most of the Mg^{2+} is substituted by Fe^{2+}, along with smaller amounts of Fe^{3+}, Mn^{2+}, and Ti^{4+}. Additionally, about a third of the Ca^{2+} is replaced by a mixture of Na^+ and K^+.

Silicon, a small atom with an electron configuration of [Ne] $3s^2$ $3p^2$, occupies a position in the periodic table just below carbon. Similar to carbon, it forms sp^3-hybrid bonds, with a tetrahedral arrangement. In the context of silicates, each silicon atom typically links with oxygen atoms to create $[SiO_4]$ tetrahedra. These bonds exhibit exceptional strength, and the silicon-oxygen tetrahedra are remarkably stable, with minimal variation in size. The Si-O distances consistently hover around 0.162 nm, while the O-O distances remain close to 0.27 nm. From an ionic perspective, the $[SiO_4]$ tetrahedral group carries a net charge of -4, denoted as $[SiO_4]^{4-}$.

These $[SiO_4]$ tetrahedra serve as the basic structural unit in silicates, governing the field of silicate chemistry and physics. They can exist as standalone units or can be connected to form $[SiO_4]$ chains, sheets, or condensed three-dimensional networks. In all of these structures, only the vertices of the tetrahedra are shared, with no sharing of edges or faces. As a simplified classification, silicates can be divided into three primary groups, each of which is elaborated upon in subsequent sections.

As an initial approximation, one can categorize silicates into three distinct groups, each of which is elaborated on in the subsequent sections.
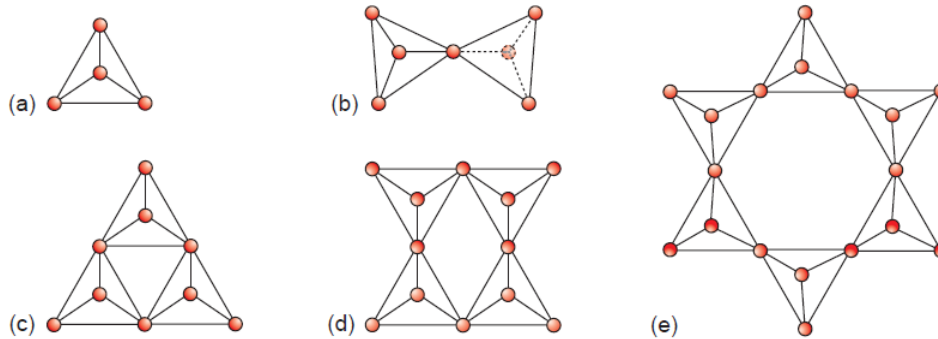
IV.2.1. Isolated silicate groups

Silicate minerals with three-dimensional structures with isolated silicate groups are commonly referred to as ionic silicates, as indicated in Table IV.1. The $[SiO_4]$ tetrahedra exhibit the capability to assemble into the following configurations: (a) isolated $[SiO_4]^{4-}$ units; (b) pairs $[Si_2O_7]^{6-}$; (c) three-membered rings $[SiO_9]^{6-}$; (d) four-membered rings $[Si_4O_{12}]^{8-}$; (e) six-membered rings $[Si_6O_{18}]^{12-}$ (as depicted in Figure IV.1).

IV.2.2. Chain or sheet silicates

Silicates that incorporate chains or sheets of silicate tetrahedra are commonly referred to as extended anion silicates. Within this category, there exists a vast array of compounds, which are valuable mineral. Even the most basic structural unit, a single chain of tetrahedra connected at their corners (as shown in Figure IV.2a), can adopt multiple distinct configurations. The chemical formula for a single chain is represented as $[SiO_3]^{2-}$, giving rise to compounds with the formula $MSiO_3$, which are known as pyroxenes. Two individual pyroxene chains can combine by connecting half of their unoccupied vertices, resulting in the formation of a double chain with the formula $[Si_4O_{11}]^{6-}$ (as depicted in Figure IV.2b). These double chains are encountered in amphiboles, a group that includes various asbestos forms. Linking the remaining unoccupied vertices along the amphibole chains leads to the creation of single silicate layers (illustrated in Figure IV.3a and b), and connecting the free vertices located at the apex of each tetrahedron gives rise to double silicate layers (as shown in Figure IV.3c).

Table IV.1: A silicate structures' summery

Structure	Formula	Hardness Mohs	Examples
Isolated			
Monomer	$[SiO_4]^{4-}$	8–5	Mg_2SiO_4, forsterite (*olivines*)
			$Ca_3Cr_2(SiO_4)_3$, uvarovite (*garnets*)
Dimer	$[Si_2O_7]^{6-}$	5	$Sc_2Si_2O_7$, thortveitite
3-ring	$[Si_3O_9]^{6-}$	7–4	$BaTi(Si_3O_9)$, benitoite
4-ring	$[Si_4O_{12}]^{8-}$	7–4	$Ca_3Al_2(BO_3)(Si_4O_{12})(OH)$, axinite
6-ring	$[Si_6O_{18}]^{12-}$	6–4	$Be_3Al_2(Si_6O_{18})$, beryl
			$NaMg_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$, tourmaline
Chains			
Single	$[SiO_3]^{2-}$	7–4	$MgSiO_3$, enstatite (*pyroxenes*)
Double	$[Si_4O_{11}]^{6-}$	5	$Ca_2Mg_5Si_8O_{22}(OH)_2$, tremolite (*amphiboles*)
Sheets			
Single silicate layer	$[Si_2O_5]^{2-}$	3–1	$Na_2Si_2O_5$, nitrosilite
Double silicate layer	$[SiO_2]$	3–1	$CaAl_2Si_2O_8$ (half Si replaced by Al), dmisteinbergite
Single silicate + single hydroxide layer	$[Si_2O_5]^{2-} + [OH]^-$	3–1	$Al_2(OH)_4Si_2O_5$ kaolinite (*clays*)
			$Mg_3(OH)_4SiO_5$ chrysotile (*clays*)
Double silicate + single hydroxide layer	$[Si_4O_{10}]^{4-} + [OH]^-$	3–1	$Al_2(OH)_2Si_4O_{10}$, pyrophyllite (*clays*)
			$Mg_3(OH)_2Si_4O_{10}$, talc (*clays*)
	$[(Si,Al)_4O_{10}]^{n-} + [OH]^-$	3–1	$KAl_2(OH)_2Si_3AlO_{10}$, muscovite (*micas*)
			$KMg_3(OH)_2Si_3AlO_{10}$, phlogopite (*micas*)
Network			
Silicate	$[SiO_2]$	8	SiO_2, quartz
Aluminosilicate	$[(Si,Al)_4O_8]$	7–5	$KAlSi_3O_8$, orthoclase (*feldspars*)

Figure IV.1: Corner-linked $[SiO_4]$ units found in ionic silicates: (a) isolated (SiO_4); (b) (Si_2O_7); (c) (Si_3O_9); (d) (Si_4O_{12}); (e) (Si_6O_{18}).

IV.2.3.   Network silicates

In these minerals, the $[SiO_4]$ tetrahedra form a three-dimensional covalent network by connecting through all their vertices. This network can assume various structures, exemplified by the different polymorphs of silica, SiO_2, with quartz being the most prevalent. When aluminum substitutes some of the silicon atoms within this framework, the structure acquires a negative charge, which is

balanced by the incorporation of cations into the network. This gives rise to a diverse group of minerals known as aluminosilicates. Among them, feldspars, a significant component of many robust rocks, play a prominent role, as do zeolites and ultramarines, all of which hold substantial industrial significance.
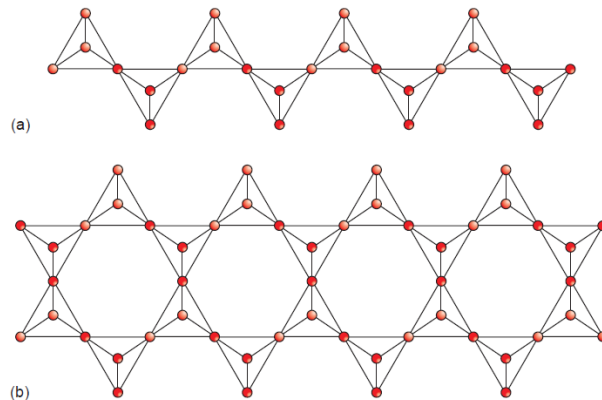

Figure IV.2: (a) Single chain (SiO_3) strings, found in pyroxenes. (b) Double-chain (Si_4O_{11}) strings found in amphiboles.
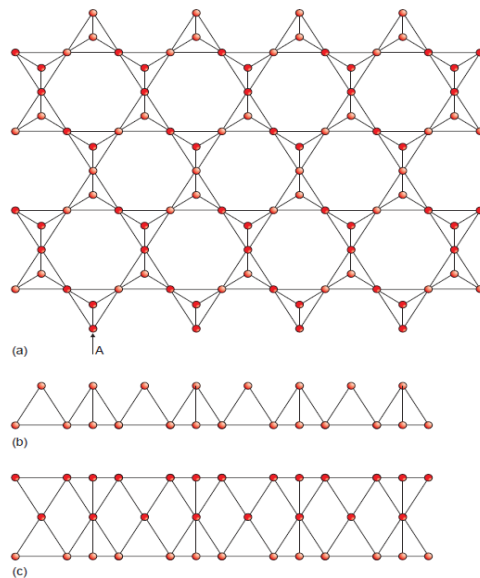

Figure IV.3: (a) A single sheet of corner-linked (SiO_4) tetrahedra. (b) The same sheet viewed along A. (c) Double sheets formed by joining two layers of the type shown in (a) by the free tetrahedral vertices, one over the other, viewed along A.

IV.3.   Non-silicate ceramics

Many non-silicate ceramics, excluding those with silicon, and numerous carbides and nitrides can be conceptualized, to some degree, as ceramics without silicon. The halite structure is adopted by many significant ceramics, including oxides like MgO and NiO, as well as carbides and nitrides such as TiC and TiN. Oxides typically function as ionic insulators, whereas carbides and nitrides exhibit metallic properties.

Aluminium oxide, known for its high-temperature resistance, finds application in laboratory furnace-ware. Several other oxides, such as Fe_2O_3 and Cr_2O_3, share a similar structure. This structure is best described as a hexagonal close-packed array of oxygen ions, with Al^{3+} ions arranged systematically over two-thirds of the available octahedral sites (Figure IV.4). Some well-known gemstones are composed of Al_2O_3 doped with trace amounts of transition metal impurities. Ruby's color, for instance, is attributed to approximately 0.5% Cr^{3+} substituting for Al^{3+}, while sapphire contains a small quantity of Ti^{4+} and Fe^{2+} substituted for Al^{3+}.

Zirconia, also known as ZrO_2, holds significance in ceramics due to its ability to endure high temperatures. At room temperature, its structure consists of irregular polyhedra, formed by seven oxygen ions surrounding each Zr^{4+} cation within a monoclinic unit cell. When the temperature reaches around 1100 °C, the unit cell undergoes a transformation to a tetragonal structure, marked by the increased regularity of coordination polyhedra. Upon reaching temperatures of approximately 2300 °C, the structure further transforms into a cubic form, adopting the CaF_2 structure (refer to Figure IV.5). In this configuration, each Zr^{4+} ion is encircled by eight oxide ions positioned at the corners of a cube. The overall arrangement can be envisioned as an array of ZrO_8 cubes, interconnected by edges in a three-dimensional checkerboard pattern. Notably, the monoclinic to tetragonal crystallographic transformation at around 1100 °C involves a substantial volume change. This change leads to cracking and weakness in

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ceramic components, rendering the use of pure zirconia impractical for certain high applications. Nevertheless, the cubic structure can be maintained by introducing impurities like calcia (CaO), wherein Ca^{2+} ions replace Zr^{4+} ions in the framework. This leads to the preservation of a cubic configuration in calcia-stabilized zirconia, spanning from room temperature up to its melting point, exceeding 2300 °C, facilitating trouble-free high-temperature applications.
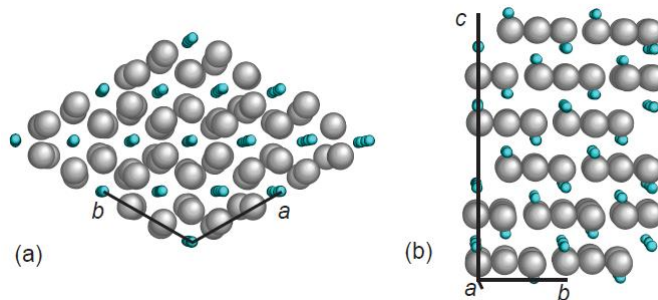
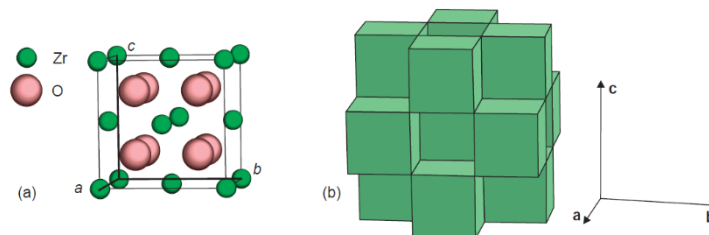**Figure IV.4:** The structure of Al_2O_3: (a) projection close to [001]; (b) projection close to [100].

Figure IV.5: The cubic ZrO_2 structure: (a) a single unit cell; (b) the structure as a stacking of (ZrO_8) cubes linked by edge-sharing.

IV.4.   The preparation and processing of ceramics

The distinctive properties of ceramics emerge during the manufacturing process. Ceramics are crafted through high-temperature firing methods, instigating chemical reactions that culminate in the final material. Traditional ceramics primarily consist of blends of clays, silica (commonly obtained as flint), and feldspars, particularly $K_2Al_2Si_6O_{16}$ and Na_2Al_2-Si_6O_{16}. Basic structural items like bricks and pipes are directly fashioned from suitable clay of lower quality. In

contrast, superior ceramics like porcelain are meticulously produced using precise quantities of specific clay, flint, and feldspar. The amalgamation of these three key components has given rise to the term "triaxial whitewares" for these materials.

Traditional ceramics, based on clay, are initially shaped using traditional pottery methods or automated processes. The formed shapes undergo heating to 1000°C or beyond. At these elevated temperatures, the clays undergo an initial reaction, losing water and hydroxyl ions in the process. The remaining residues react, yielding a combination of new phases, including glasses. Substantial shrinkage typically takes place during these reactions, making it challenging to achieve a precise size and shape for the final object.

Engineering ceramics and electro-ceramics typically exist as pure single phases. The manufacturing process involves milling components to create a fine powder, shaping it through pressing, and ultimately subjecting it to a crucial firing step. This third phase involves intricate heating cycles. Initially, the material is heated at a low temperature, typically between 100–400 °C, to eliminate water and burn off the binder (an organic material used to bind the dry grains together). In subsequent stages of processing, the material undergoes heating to a final temperature exceeding 1000 °C. This high temperature is essential for sintering the particles and facilitating any chemical reactions. During this final stage, some components may melt, and in specific cases, such as porcelain, the outcome includes the formation of glass, a process known as vitrification.

Durable ceramic coatings can be applied to metallic components by subjecting the metal to elevated temperatures within a suitable gaseous environment. During this process, a reaction occurs at the metal surface, leading to the diffusion of atoms from the gaseous component into the surface layer. For instance, heating titanium in a nitrogen gas atmosphere induces the formation of a robust layer of titanium nitride (TiN) on the surface, enhancing its hardness.

IV.5.   The principal properties of ceramics

The fundamental characteristics of ceramics originate from the interplay of chemical bonding and the atomic defects and microstructure that emerge during the manufacturing process. The bonding, whether categorized as ionic or covalent, is robust, contributing to the chemical inertness and frequently refractory nature (stability at high temperatures) of these solids. Refractory ceramics find extensive applications in furnaces and other high-temperature apparatus. Moreover, these ceramics serve both externally, safeguarding the outer surfaces of space vehicles and satellites, and internally within rocket motors.

Basic ceramics exhibit subpar thermal and electronic conductivity due to the absence of free electrons. Nonetheless, the chemical versatility of ceramics enables selective doping with additional atoms. Specifically, introducing transition metal or lanthanoid ions through doping results in ceramics displaying a diverse range of optical, electronic, and magnetic properties. This method allows the transformation of insulators, for instance, into superconductors.

Ceramics exhibit limited deformation at ordinary temperatures due to the formidable task of breaking strong chemical bonds, and unlike metals, the movement of dislocations is significantly impeded. Typically, applied stress leads to brittle fracture, especially when subjected to impact. The brittleness of ceramics, for the most part, stems not primarily from bonding or dislocation density but from microstructural factors. Surface flaws contribute to the catastrophic failure of many ceramics when subjected to flexural forces. Weaknesses in the form of voids, pores, large grains, and foreign inclusions in the structure, resulting from chemical reactions during high-temperature fabrication, are significant contributors.

While ceramics have a relatively low tensile strength and are prone to fracture under tension, they exhibit increased strength under compression. This,

combined with their robust bonding, imparts hardness to ceramics, rendering them suitable for applications such as abrasives, cutting tools, and hard coatings.
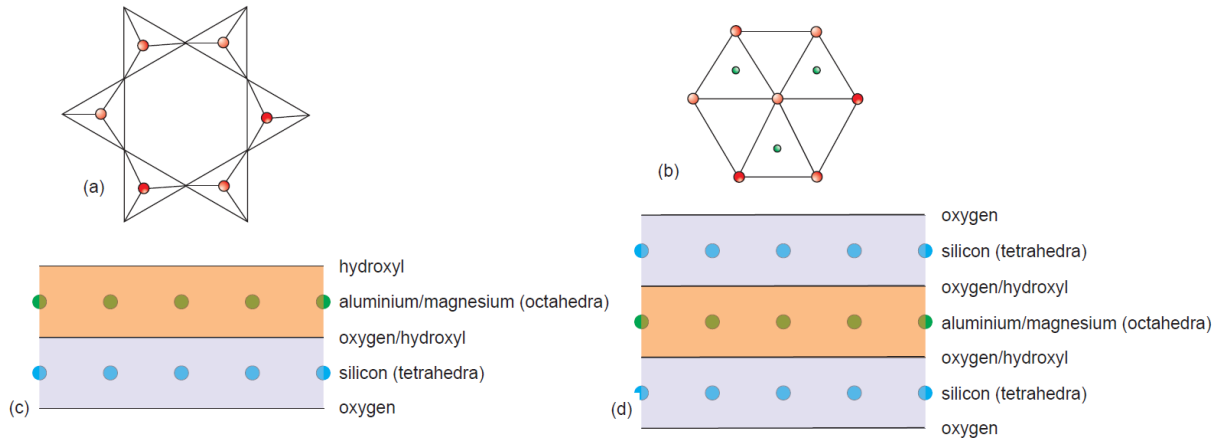

hydroxyl
aluminium/magnesium (octahedra)
oxygen/hydroxyl
silicon (tetrahedra)
oxygen

oxygen
silicon (tetrahedra)
oxygen/hydroxyl
aluminium/magnesium (octahedra)
oxygen/hydroxyl
silicon (tetrahedra)
oxygen

Figure IV.4: The structure of clays and related minerals: (a) a single layer of corner-linked (SiO_4) tetrahedra (the upper layer of apical oxygen atoms are drawn as spheres); (b) a basal close-packed layer of oxygen atoms in $Mg(OH)_2$ or $Al(OH)_3$ (large spheres), with cations in the octahedral sites above the layer (small spheres); (c) a composite layer formed by uniting a single silicate layer as in (a) and a single hydroxide layer as in (b); (d) a composite sandwich structure formed by uniting two silicate layers as in (a), with a single hydroxide layer as in (b).

Exercise:
1. What are ceramics?
2. How are ceramics characterized?
3. What does Isomorphous replacement mean?
4. What is the difference between silicate ceramics and non-silicate ceramics?
5. What is the basic structural unit in silicates?
6. Cite the three groups of silicates.
7. Draw the possible configurations of tetrahedra SiO_4 unit in isolated silicate group.
8. Give some examples of non-silicate ceramics.
9. What is the origin of ceramic characteristics?
10. What does refractory ceramics mean?
11. Why do ceramics show subpar thermal and electronic conductivity?

Chapter V: Silicate glasses

V.1. Introduction

Glasses encompass non-crystalline materials, with a predominant presence of oxides, although specialized variants like metallic glasses are gaining significance. Within this context, glass is defined as a robust, transparent, and corrosion-resistant substance, primarily composed of silica, SiO_2, referred to as silicate glasses. Naturally occurring silicate glasses, such as obsidian (a volcanic rock characterized by its black hue due to iron oxide impurities), pumice (a glassy froth), flint, and opal, exhibit characteristic glass properties of hardness and brittleness.

The production of silicate glass holds historical importance, marking an early stage in civilization. Egyptians crafted faience thousands of years ago using molded sand coated with natron, a mineral residue from the flooding of the Nile River, consisting mainly of calcium carbonate, sodium carbonate, common salt, and copper oxide. The heating of the object to approximately 1000 °C led to the alkali coating reacting, forming a glassy exterior with a blue tint from the copper oxide.

Advances in glass technology were closely guarded secrets within medieval guilds, and only in more recent times has high-quality transparent glass become widely accessible. This transformation was initiated by the development of superior lenses in the 19th century and further accelerated by the advent of optical fiber-based communication systems in the late 20th century.

V.2. Bonding and structure of silicate glasses

The primary building block in silicate glasses is the $[SiO_4]$ group. The covalent bonds between the central silicon atom and the oxygen atoms exhibit exceptional strength, and both the liquid and solid states of silica and silicates consist of numerous $[SiO_4]$ tetrahedra. These tetrahedra connect by sharing corner oxygen atoms, forming either discrete or interpenetrating chains and rings. In the solid state, these structures are fixed, whereas in the liquid state, they undergo continuous orientation changes.

The crystallization of a liquid into a solid requires the formation of crystal nuclei. While this process is straightforward for metals due to the quick packing of spherical atoms into arrays, it proves challenging for silicates due to the intricate reorganization of entangled chains into an ordered crystalline arrangement. This slow nucleation process, often involving bond breakage and tetrahedra rearrangement, can result in the formation of glass even at slow cooling rates. Zachariasen proposed the structure of a silicate glass in 1932, envisioning it as an irregular intertwining of chains of corner-linked [SiO$_4$] tetrahedra to create a loose, random network (Figure V.1).

Although commonly referred to as a supercooled liquid, it's crucial to recognize that glass is a solid lacking long-range order in its structure. This characteristic is evident when heating, as glasses lack a distinct melting point and instead gradually soften from a solid state to a viscous liquid state. The glass transition temperature, Tg, defines this transition, determined by plotting the specific volume (volume per unit mass) against temperature (Figure V.2). The glass transition temperature is not a fixed property, varying with the cooling rate, and caution is necessary due to different Tg definitions. Nevertheless, it serves as a valuable materials parameter, offering insights into the softening and working temperature of a specific glass.
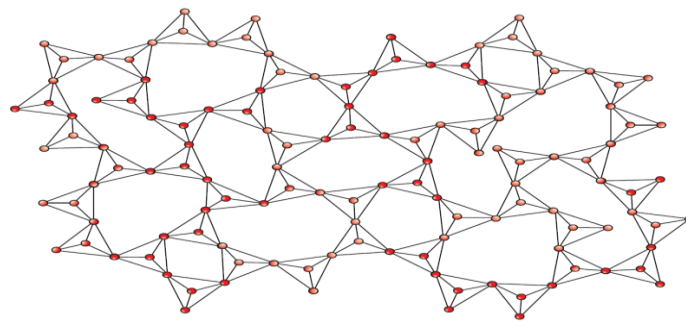

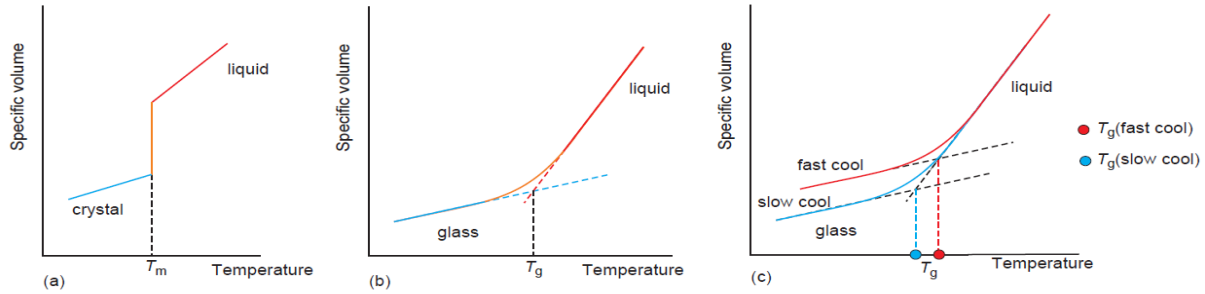**Figure V.1**: The random network model of corner linked (SiO$_4$) tetrahedra in a silicate glass.

Figure V.2: Specific volume versus temperature curves: (a) a crystalline solid, with melting point Tm; (b) a glass, with glass transition temperature Tg; (c) the effects of cooling rate on glass transition temperature.

The random network model effectively describes silicate glasses. In addition to $[SiO_4]$ tetrahedra, cations occupying tetrahedral or triangular coordination with metal–oxygen bond lengths similar to Si-O bonds can seamlessly integrate into the chains. These cations, often B^{3+}, Ge^{4+}, Al^{3+}, Be^{2+}, and P^{5+}, are termed network formers. Large cations, such as K^+, Na^+, Mg^{2+}, or Ca^{2+}, which disrupt the ability of $[SiO_4]$ tetrahedra to crystallize regularly, are known as network modifiers, enhancing glass formation. Another category includes intermediate ions with higher valence and coordination, like Ti^{4+}, Cu^{2+}, and Zn^{2+}, which affect glass properties but do not directly contribute to glass formation. It's worth noting that these categories are not mutually exclusive, and certain ions may fall into multiple categories, such as Al^{3+}, considered both a network former and an intermediate depending on its coordination.

V.3.   Glass deformation

One intriguing characteristic that sets glass apart from metals and crystalline ceramics is its ability to undergo deformation in a semi-molten state through traditional methods like glass-blowing. This unique property arises from the fact that glasses exhibit a high viscosity, resembling very viscous liquids at moderate temperatures. In this semi-molten state, they can be easily shaped using conventional techniques and retain the desired form upon cooling.

The viscosity of glass, particularly its dependence on temperature (refer to Figure V.3 a), serves as a crucial physical parameter. This relationship defines the temperature ranges within which the glass can be effectively manipulated, as outlined in Table V.1. The working range of a glass refers to the viscosities within which normal processing occurs, typically falling between viscosity values of 10^3 and $10^{6.6}$ Pa.s. It's noteworthy that the temperature at which a specific glass achieves the necessary viscosity is contingent upon its composition, which, in turn, is linked to its intended application.
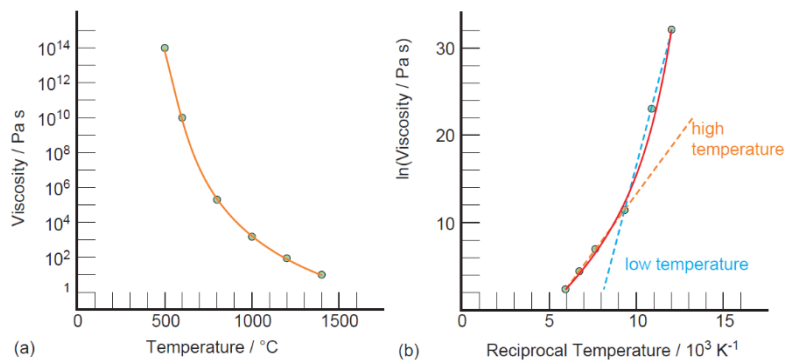

Figure V.3: (a) Viscosity versus temperature for a typical soda-lime glass. (b) Plot of ln (viscosity) versus reciprocal temperature for the same glass.

Table V.1: Glass viscosity

Glass condition	Approximate viscosity/Pa s	Comment	Approximate temperature/°C for soda-lime glass
Melting temperature	10	Glass becomes fluid and a homogeneous melt is achievable	1450
Working point	10^3	Glass easily deformed, but retains its shape	1000
Softening point	$10^{6.6}$	Glass deforms under its own weight	700
Annealing point	10^{12}	Residual stress in a thin plate can be removed in 15–20 minutes	550
Strain point	$10^{13.5}$	Fracture–plastic deformation boundary	500

Given the practical significance of viscosity, numerous efforts have been made to establish a mathematical equation describing the correlation between viscosity and temperature. One of the simplest formulations is the Arrhenius equation:

$$\eta = \eta_0 exp\left(\frac{E}{RT}\right)$$

In this expression, η represents viscosity, η_0 is a constant, E denotes the energy associated with viscous flow (referred to as activation energy), R is the gas constant, and T signifies the temperature in Kelvin. This formula characterizes activated processes, wherein a transformation occurs only when the involved elements surpass an energy barrier. The confirmation of Arrhenius behavior in such reactions is established through a graphical representation of $ln\ \eta$ against $1/T$.

$$ln\ \eta = ln\ \eta_0 + \frac{E}{RT} \qquad (1)$$

The storyline is expected to follow a linear trajectory with a slope of E/R. Materials that adhere to equation (1) are described as exhibiting Arrhenian behavior. However, this behavior is typically not observed in glasses, which demonstrate non-Arrhenian characteristics. The plot of natural logarithm of η versus the reciprocal of temperature (1/T) often forms a smooth curve, although the low-temperature and high-temperature segments of the graph, when considered independently, may reasonably conform to equation (1) (see Figure V.3 b). Notably, the high-temperature slope is generally lower than that of the low-temperature section.

To address the limitations of the Arrhenius equation, various alternative equations have been proposed. Among these, the Vogel-Fulcher-Tamman equation, also known as the Vogel-Fulcher equation, is the most widely utilized.

$$\eta = A\ exp\left(\frac{B}{T - T_0}\right)$$

The relationship is established through the use of empirical constants A, B, and T_0, where T represents the temperature in Kelvin (K).

$$ln\ \eta = ln\ A + \left(\frac{B}{T - T_0}\right)$$

Viscosity is commonly depicted on an Angell plot (Figure V.4), illustrating *log η* against Tg/T. This representation is essentially a scaled adaptation of an Arrhenius plot (See Figure V.3 b.) The (straight) diagonal line in the figure corresponds to the ideal Arrhenius behavior. Curves positioned to the right of this diagonal are indicative of fragile liquids, while those on the opposite side of the diagonal represent strong liquids. The fragility of a liquid is a measure of its deviation from Arrhenian behavior. It is associated with various interatomic interactions contributing to viscosity, including weak bonding such as van der Waals and hydrogen bonding, but it is not solely an expression of chemical bonding. For instance, silica falls into the fragile region despite having strong covalent SiO bonds within the SiO_4 tetrahedra.
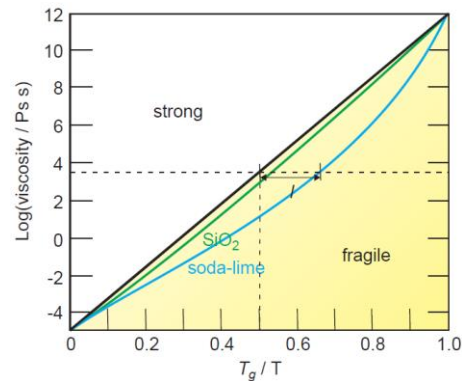

Figure V.4: Angell plot: strong liquids are to the upper left and fragile liquids to the lower right; curves are for silica and a soda-lime glass. The line *l* is a measure of the departure of a glass (here soda-lime glass) from Arrhenian behavior, used in determination of the kinetic fragility, $F_{1/2}$.

Quantifying fragility involves measuring the slope of the Arrhenius plot as the temperature approaches the glass transition temperature, Tg.

$$m = \left(\frac{d \log \eta}{d\left(T_g/T\right)} \right)_{T \approx T_g}$$

Here, m is referred to as the fragility, or alternatively, the steepness index. For a liquid following the Arrhenius law, the value of m is determined by the slope of

the diagonal on the Angell plot, which is equal to 17. Obtaining the value of m from experimental data is not always straightforward. As an alternative, a kinetic fragility, denoted as F½, has been introduced. The F½ value is calculated as follows:

$$F_{1/_2} = 2\left(\frac{T_g}{T} - 0.5\right)$$

The point where a horizontal line intersects the necessary glass curve at the midpoint of the logarithmic height (Tg/T) signifies the value. The enclosed quantity represents the parameter 1 (as illustrated in Figure V.4 for soda-lime glass), and the inclusion of the factor 2 ensures that F½ values are confined within the range of 0 to 1. The significance of fragility extends beyond silicate glasses, finding applications in diverse scientific domains, such as the examination of water-based solutions and pharmaceutical products.

V.4.   Strengthened glass

Glass exhibits strength under compression but is notably weak in tension. Freshly drawn glass fibers, for instance, boast greater strength than steel; however, exposure to water vapor in the atmosphere leads to a significant decline in fiber strength due to surface attacks, commonly attributed to small flaws known as Griffith's flaws. Under tension, these flaws induce cracks that result in material fracture. Various methods employed to reinforce glass aim to impede crack propagation within the solid.

Tempered glass, for example, possesses roughly four times the strength of regular glass, breaking into small, blunt fragments instead of sharp shards upon fracture. The strengthening process involves rapidly cooling the hot glass surface using air jets. Initially, the glass is shaped, and any surface flaws or rough edges are eliminated through grinding and polishing. Subsequently, the glass is heated to 620 °C. High-pressure air jets, arranged in a predetermined pattern, swiftly cool the surface within a few seconds. During this quenching process, the exterior of the glass sheet solidifies as its temperature drops below the glass

transition temperature. However, the interior, cooling at a slower rate, remains above this temperature. As the interior cools, it tends to contract away from the solid outer surfaces, inducing tension in the center while subjecting the outer surfaces to compression. This opposing interplay of tensile and compressive stresses serves as the strengthening mechanism. Since glass commonly fails due to surface crack generation, a surface under compressive force is notably more resistant to breakage. Carefully controlled stress patterns, tailored to the material's intended use, are generated. These stress patterns may manifest as colored shapes in the windshield of a car when exposed to sunlight, especially if the driver wears polarizing lenses.

Chemical strengthening seeks to replicate the distribution of tension and compression described earlier but employs chemical methods. While effective, these methods are generally more costly than air-cooling and are predominantly applied in situations where cost is a secondary consideration. The underlying principle involves selectively substituting certain metal ions in the glass to induce tension or compression. For instance, immersing a soda-lime glass in molten potassium nitrate results in the replacement of Na^+ on the glass surface with the larger K^+. This substitution generates surface compressive stress and internal tensile stress, enhancing the glass's strength. This technique finds application in manufacturing aircraft glazing and lenses. Similarly, replacing Na^+ with the smaller Li^+ induces surface tension and interior compression, making it suitable for producing glass used as laser materials.

V.5.   Glass-ceramics

A glass-ceramic is a solid predominantly composed of crystals, resulting from the partial devitrification (crystallization) of a glass object shaped as desired. These materials are essentially composites, containing both crystals and some glass, leveraging the production ease of glass while enhancing thermal and mechanical properties significantly. The initial step involves crafting the object from a suitable glass, followed by a controlled thermal treatment to transform it into a largely crystalline structure of the same shape and size. This process

induces the precipitation of crystal nuclei, crystal growth, and the development of an almost fully crystalline final product (see Figure V.5). It is crucial for the crystallization to occur in a glass with sufficient viscosity to prevent sagging or distortion during the transformation.
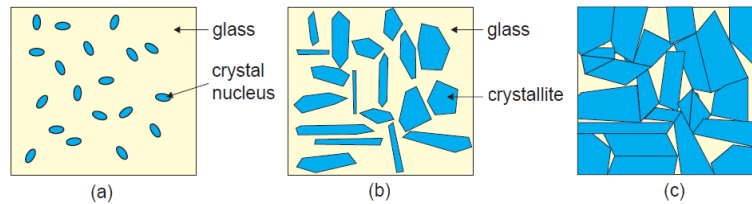

Figure V.5: Crystal nucleation (a) and crystal growth (b, c) in a glass ceramic.

The key factors in glass-ceramic production are the composition of the melt and the microstructure of the final product, which are interconnected. The composition dictates the substance's ability to form a glass with the correct viscosity and workability since the initial solid is entirely glassy. It also controls the formation of nuclei in the glass and the types of crystals that can grow. The microstructure is influenced by the crystal habit, impacting the final solid's properties.

Excellent mechanical properties are achieved due to the presence of interlocking crystals, impeding the propagation of surface flaws through the solid. Meanwhile, optimal thermal properties result from crystals with very low coefficients of expansion, enhancing resistance to thermal shock. The optical properties can be manipulated, with transparent or translucent outcomes depending on crystal dimensions.

Transparent ultra-fine-grained glass-ceramics, microstructurally speaking, consist primarily of the high-temperature form of quartz. Starting with a silica melt containing ZrO_2, TiO_2, Al_2O_3, and MgO, the material is shaped and heat-treated, forming $ZrTiO_4$ crystals as nucleation sites, followed by the growth of high-temperature quartz crystals. The presence of aluminum and magnesium in the crystals stabilizes the structure. The final solid comprises crystals less than

60 nm in size, along with residual glass, providing transparency, resistance to thermal shock, and strength.

Different compositions and heat treatments yield glass-ceramics with diverse microstructures, influencing properties significantly. For instance, materials used in rocket nose cones may consist mainly of cordierite, an aluminosilicate with low thermal expansion. Machinable glass-ceramics, featuring interlocking plates of mica, find use in precision ceramic components, ensuring stability during machining processes.

Exercise:

1. The glass transition temperature marks the point at which:

    a. A glass transforms from a solid to a viscous liquid.
    b. The glass can be moulded and blown.
    c. The glass becomes stable.

2. A glass ceramic is:

    a. A glass processed at high temperatures.
    b. A transparent ceramic.
    c. A ceramic containing both crystals and glass.

Chapter VI : Polymers

VI.1.   Introduction

Polymers are chain-like molecules formed by connecting repeating monomer units, with carbon-based backbones adopting various configurations. Polymer nomenclature evolved from informal to systematic, with structure-based and source-based naming systems. Polymers, including synthetic (e.g., nylon) and natural (e.g., DNA), play vital roles in living organisms. They fall into thermoplastics, thermosetting materials, and elastomers. Polymer properties depend on chain details and interactions, leading to diverse structures like crystals or amorphous masses. Despite their reputation for electrical insulation, advancements have produced polymers with metallic conductivity surpassing copper, and some function as electrolytes in batteries.

VI.2.   Polymer formation

Polymers were initially categorized as addition or condensation based on the polymerization reaction. These classifications, rooted in organic chemistry, have shifted to focus on the polymerization mechanism. To connect monomers, each end must become chemically reactive, often by breaking chemical bonds. Ethene (ethylene) is a simple starting point for understanding this process.

$$CH_2 = CH_2$$
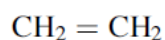
In a schematic representation, ethene monomers connect through an addition reaction by opening double bonds and linking broken bonds (Figure VI.1). The resulting polymer is polyethylene or polythene.

$$[CH_2\text{-}CH_2]_n$$
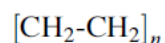
The polymer chain of polythene, with variable 'n' in the range of thousands, is composed of (CH_2) units forming sp3-hybrid bonds (Figure VI.2). Carbon-carbon bonds allow free rotation, resulting in coiling into ordered or disordered regions. Polythene lacks a precise chemical formula, with the quantity of (CH_2) units influenced by preparation conditions. Physical properties vary between polymers with lower and higher average values of 'n'.

Polymers with connections can be formed by substituting hydrogen atoms in the ethene monomer with a chemical group denoted as X (refer to Table VI.1). This transforms the monomer's formula to $CH_2=CHX$ upon substitution. Despite variations in X's size and position, the fundamental principle of polymerization remains unchanged, with adjustments to specifics.

Figure VI.1: The polymerisation of ethene (ethylene) schematic: (a) a single monomer molecule; (b) double bond opening; (c) monomer linkage to form the polymer chain.
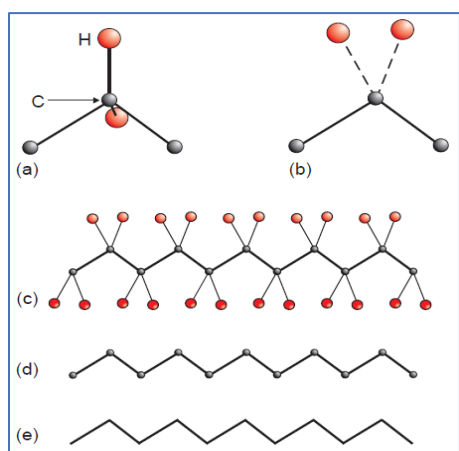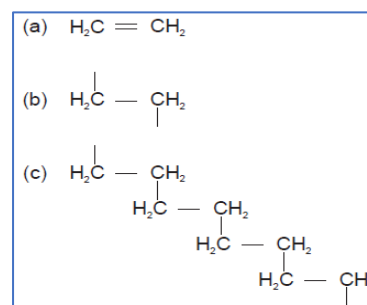

Figure VI.2: (a, b) The structure of the CH_2 unit in a polymer chain, in two orientations. The four bonds arising at the carbon atom are arranged tetrahedrally. (c) A chain of linked CH_2 units. (d, e) Representations of the chains with H atoms omitted.

A common condensation reaction involves the combination of a carboxyl group, COOH, with a hydroxyl group, OH, resulting in the formation of a larger molecule and the release of water.

$$R - COOH + R' - OH \rightarrow R - COO - R' + H_2O$$
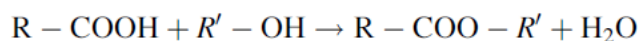
Condensation polymers, such as polyesters and thermoplastic polyamides (nylons), require monomers with two reactive groups for polymerization. Polyesters, like poly(ethylene terephthalate) or PET, form from terephthalic acid and ethylene glycol, widely used for shatterproof bottles (Figure VI.3). Thermoplastic polyamides, or nylons, result from the interaction of carboxylic acid group (COOH) and amide group (NH_2).

$$R - COOH + R' - NH_2 \rightarrow R - CON - R' + H_2O$$
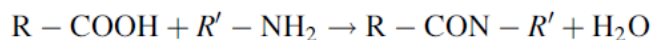
Table VI.1: Addition polymers

Monomer source	Polymer formula	Names	Uses
$CH_2=CH_2$ (ethene, ethylene)	$(CH_2\text{-}CH_2)_n$	Polyethylene, polythene, PE	Squeeze bottles, food bags, dishes, insulation, coatings
$CH_2=CH\,Cl$ (vinyl chloride)	$(CH_2\text{-}CHCl)_n$	Poly(vinyl chloride), PVC	Pipes, floor covering, insulation, adhesives, films, credit cards
$CH_2=CCl_2$ (vinylidene chloride)	$(CH_2\text{-}CCl_2)_n$	Poly(vinylidene chloride)	Food wraps, fibres, cling film
$CH_2=CH\,CH_3$ (propylene)	$(CH_2\text{-}CH\,(CH_3))_n$	Polypropylene, PP	Pipes, valves, carpets
$CH_2=CH\,C_6H_5$ (styrene)	$(CH_2\text{-}CH\,(C_6H_5))_n$	Polystyrene, PS	Jugs, cups, packaging, styrofoam, appliance parts
$CH_2=CH\,CN$ (acrylonitrile)	$(CH_2\text{-}CH\,(CN))_n$	Polyacrylonitrile, PAN, Orlon, Acrilan	Fabrics, carpets, high-impact plastics
$CH_2=CH\,COOCH_3$ (vinyl acetate)	$(CH_2\text{-}CH\,(CH_3\,COO))_n$	Poly(vinyl acetate), PVA	Wood adhesives, paper coatings, latex paints
$CF_2=CF_2$ (tetrafluoroethene)	$(CF_2\text{-}CF_2)_n$	Poly(tetrafluoroethylene), PTFE, Teflon	Non-stick coating, electrical insulation, bearings
$CH_2=C(CH_3)COOCH_3$ (methyl methacrylate)	$(CH_2\text{-}C(CH_3)COOCH_3)_n$	Poly(methyl methacrylate) Perspex, Lucite, Plexiglass	Substitute glass, acrylic paints, pipes
$CH_2=CH-CH=CH_2$ (1,3-butadiene)	$(CH_2\text{ - }CH-CH\text{ - }CH_2)_n$	Polybutadiene, buna rubber	Tyres, hoses, pond liners

with R and R' denoting distinct carbon chains. To create a polymer, each monomer must possess reactive groups at both ends of the molecule. Illustratively, the formation of the most prevalent type of nylon, nylon 66, exemplifies this process (Figure VI.4a). The term "nylon 66" signifies the presence of six carbon atoms in each segment of the polymer's repeat unit.

Figure VI.3: The production of the polyester PET schematic. The linking of the terephthalic acid and ethylene glycol molecules occurs at 210°C, and polymerisation and regeneration of ethylene glycol at 270°C.
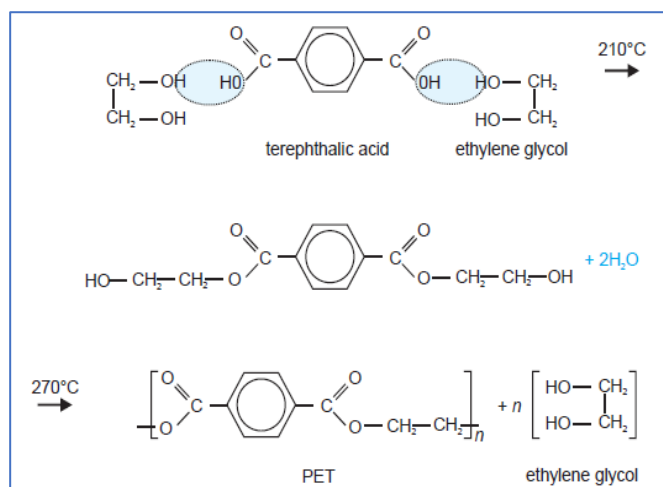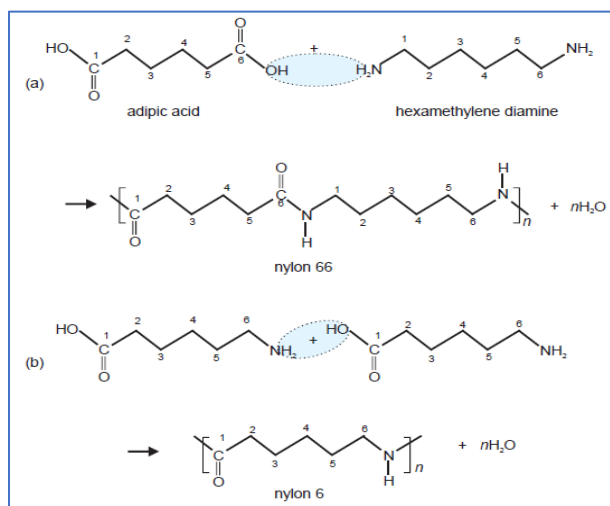
Figure VI.4: Formation of nylon schematic: (a) nylon 66; (b) nylon 6. The carbon skeleton of the polymer chain is drawn as a zigzag and the number of carbon atoms in the polymer chain between nitrogen atoms is indicated.

Amino acids, with a structure of $HOOCRNH_2$, undergo polymerization to create nylon, exemplified by nylon 66 (Figure VI.4b). Nylon 6, a counterpart, is produced from e-caprolactam. The even–even and odd–odd concept extends to nylons like nylon 44 and nylon 55, impacting electrical properties. A related reaction yields thermosetting polymers like epoxy resins. The epoxy group facilitates monomer linking, forming a cross-linked network upon resin setting. Epoxy resins, classified as typical thermosets, undergo minimal dimensional changes, making them valuable in applications such as dental fillings (Figure VI.5).

Figure VI.5: Epoxy resins: (a) the epoxy group; (b) a small diepoxy molecule; (c) a small polymer molecule (with n up to about 25) found in the resin part of a two-part epoxy adhesive mix; (d) a diamine linking group (catalyst). R represents a short chain of CH_2 groups.
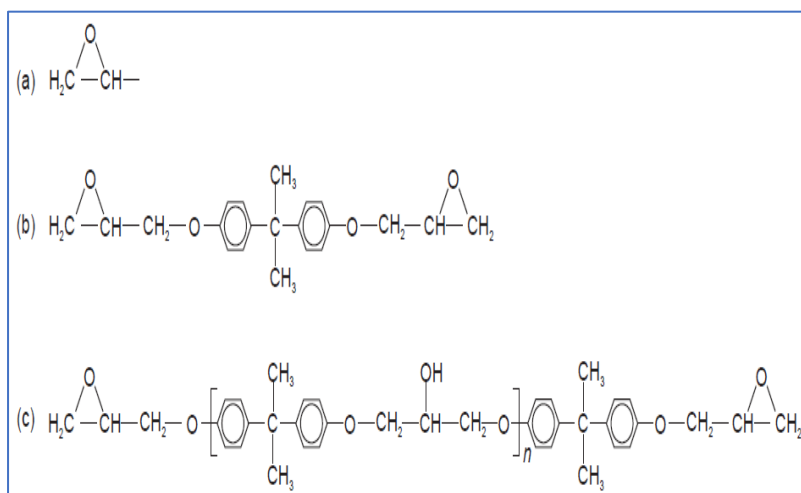
Cross-linked polymers, like epoxy resins, resist disruption, functioning as one large molecule, making them durable for various applications. Polymers, such as the polyester from phthalic acid and glycerol (Figure VI.6), can be modified for extensive cross-linking, creating a polymer used in bake-on car paints.

Figure VI.6: Reaction of molecules with several active groups can give rise to cross-linked polymers.
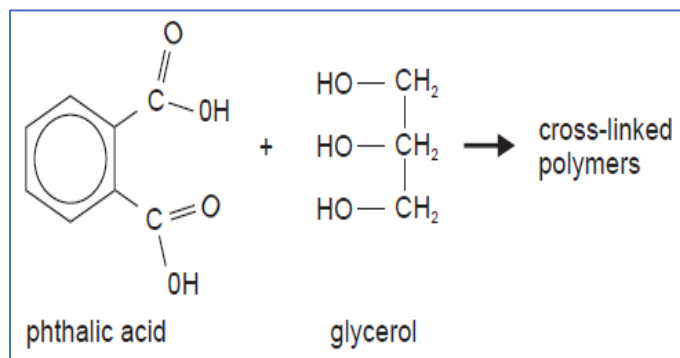
VI.3. Microstructures of polymers

While the properties of polymers are affected by their chemical composition, the primary determinant is the microstructure. Chain length, chain branching, the presence of chain side-groups (influencing chain stiffness), and the robustness of cross-links between chains are key features of polymer microstructure. The level of crystallinity in the polymer, influenced by the aforementioned factors, is equally significant. Indeed, the strength of the majority of thermoplastic polymers is highly dependent on this particular factor.

VI.3.1. Molar mass

Polymers are composed of elongated chains of varying lengths, and their characterization is not possible through a constant molar mass. In the case of cross-linked polymers, they can be conceptualized as a singular molecule, where the molar mass represents the total mass of the entity. Despite this, it is valuable to gauge the degree of polymerization or the distribution of chain lengths, often expressed as an average molar mass.

To provide a measure of the polymer's chain length or the spread of chain lengths, an average molar mass is employed. Ideally, the distribution of chain

lengths in a polymer sample follows a bell-shaped curve. Reflecting the relationship between chain length and molecule mass, this information is commonly presented as a graph depicting the number of molecules against the molar mass (refer to Figure VI.7a). Typically, the distribution deviates from a simple bell shape (refer to Figure VI.7b), and the curve's form is frequently indicative of a specific reaction mechanism.

For a statistical definition of chain length, the molar mass must be quantified. The number average molar mass, denoted as Mn, is defined as follows:

$$M_n = \sum_i x_i M_i$$

$$x_i = \frac{n_i}{\sum_i n_i}$$

Here, xi represents the fraction of the overall number of chains falling within the specified molar mass range, and ni signifies the count of molecules with a molar mass of Mi. The number average molar mass aligns with the apex of a bell-shaped distribution curve. Another metric, the weight average molar mass denoted as Mw, considers the reality that larger molecules contribute significantly to the overall mass of the sample.

$$M_w = \sum_i w_i M_i$$

$$w_i = \frac{n_i M_i}{\sum_i n_i M_i}$$

Here, wi denotes the mass fraction attributed to each specific molecule type found within the designated molar mass range.
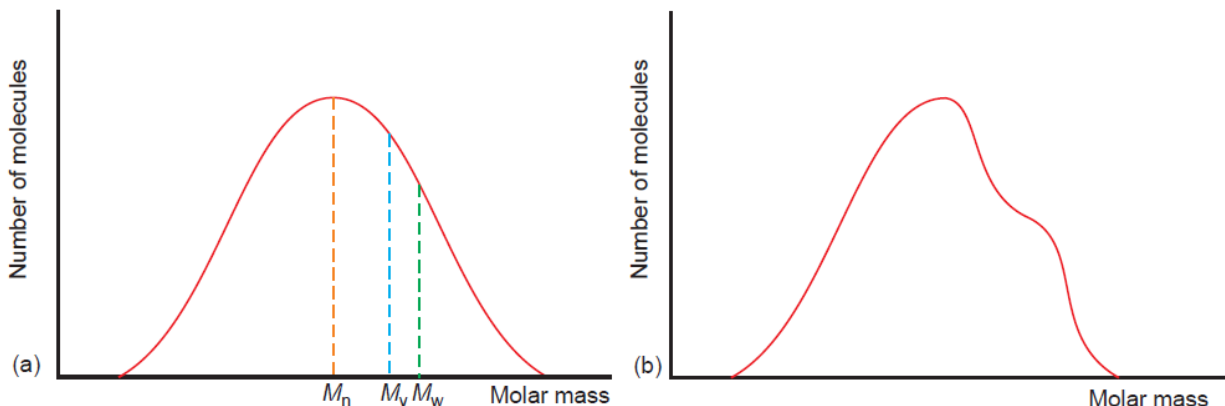
Figure VI.7: Molecular mass of a polymer. (a) Idealised distribution: Mn is the number average molecular mass,

Mv is the viscosity molecular mass and Mw the weight average molecular mass. (b) Example of a real mass distribution.

The experimental determination of molar mass is also possible. One commonly employed method involves measuring the viscosity of a polymer-containing solution. Increased viscosity suggests longer chains and a higher molar mass. The molar mass determined through this approach, denoted as Mv, falls within the range of Mn and Mw (refer to Figure VI.7a). The degree of polymerization, represented by N, corresponds to the number of monomer units in an average chain. It is calculated by dividing the molar mass by the monomer mass, denoted as m. The resulting value varies depending on the specific molecular mass values chosen.

$$N_n = \frac{M_n}{m} \quad N_w = \frac{M_w}{m} \quad N_v = \frac{M_v}{m}$$

VI.3.2.   Chain structure

Polymerization entails the breaking and reformation of numerous chemical bonds, leading to diverse molecular structures (see Figure VI.8). Chains often exhibit not only linearity but also side-branches, potentially forming crosslinks between molecules. In some cases, multiple chains may initiate growth from a

small nucleation center, branching out to create a dendritic structure. These varied molecular geometries contribute distinct physical properties to the resulting polymer.

Polyethylene, also known as polythene, represents a long-chain polymer composed of 10^4 or more ethene (ethylene) units. When these chains are relatively short and extensively branched, the material exhibits low density, a diminished refractive index, and notable flexibility albeit with reduced strength. This variant is identified as low-density polyethylene (LDPE). In contrast, high-density polyethylene (HDPE) consists of linear molecules with a molecular weight ranging between 200,000 and 500,000, resulting in significantly enhanced strength compared to LDPE. Ultra-high molecular weight polyethylene (UHMWPE), boasting a molecular weight around 5,000,000, exhibits even greater strength. The mechanical characteristics of polyethylene are further influenced by the degree of crystallization. When slowly cooled from the melt, some chains organize into crystalline regions measuring 10–20 nm in thickness. These crystalline regions, characterized by high density and refractive index, coexist with amorphous regions in most polythene, contributing to its milky appearance.
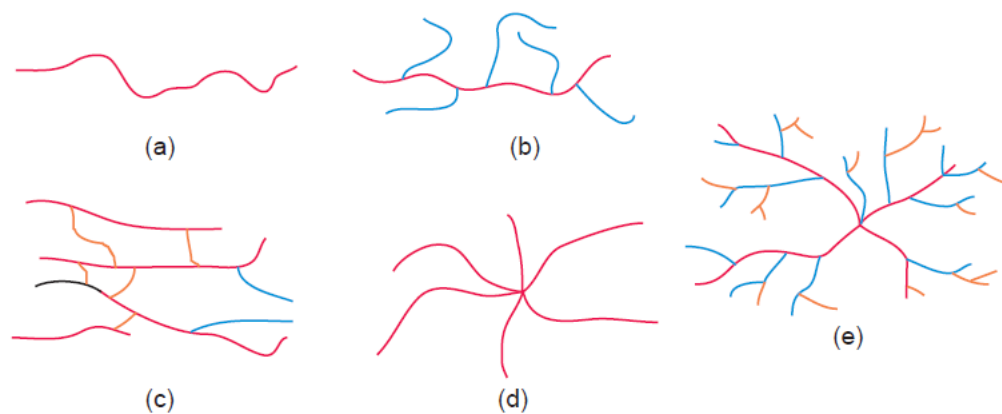

Figure VI.8: Polymer chain geometries: (a) linear; (b) branched; (c) cross-linked; (d) star; (e) dendrimer.

VI.3.3. Crystal structure

Polymers seldom exhibit straight chains; more commonly, as observed in solid polythene and similar polymers, the chains intricately fold back upon themselves, forming distinct fold lengths (see Figure VI.9a). These folded chains aggregate into blocks known as lamellae, exhibiting a regular structure akin to a crystal (Figure VI.9b). Lamellae typically result from the collaboration of various neighboring chains, as illustrated in Figure VI.9c. The segments of the chains not assimilated into the lamellae then connect one lamella to another in the partially crystalline material. During the crystallization process from a molten state, lamellae emerge in three dimensions, originating from a nucleation site to create a spherulite. This spherulite comprises spokes, referred to as lamellar fibrils, radiating outward from a common center into the amorphous interspoke regions (see Figure VI.10).

The polymer's ability to crystallize is contingent upon the specific details of its chain. For instance, the amide group, being a polar unit, establishes hydrogen bonds with the carboxyl oxygen in nylons. These intermolecular forces effectively unite the chains, resulting in a highly crystalline polymer endowed with exceptional strength.
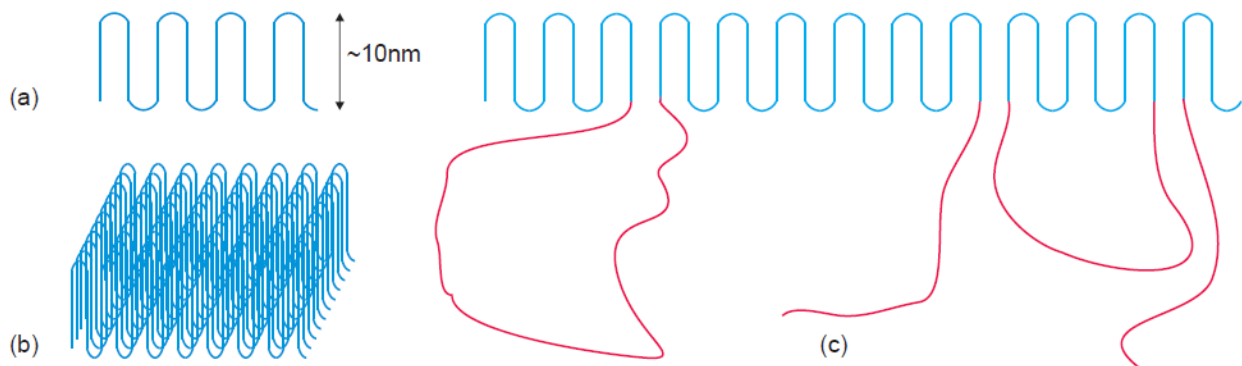

Figure VI.9: (a) Polymer chains in polyethylene fold back on themselves approximately every 10 nm. (b) Folded chains aggregate to form a lamella. (c) Lamellae can contain more than one polymer chain, or a chain folded back into the arrangement.
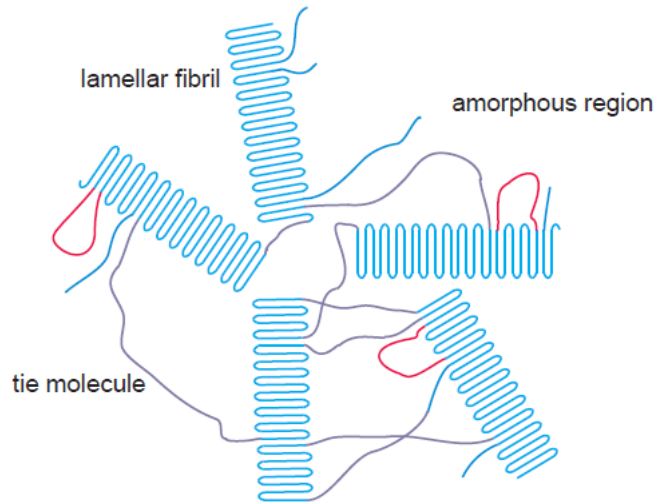
Figure VI.10: Schematic structure of a spherulite in a polymer such as polyethylene.

The determination of a polymer's crystallinity involves knowing the densities of both polymer crystals and purely amorphous material. This process mirrors the application of Vegard's law in determining the lattice parameter of a solid solution. The fraction of crystalline polymer, denoted as xc, can be calculated using the following formula:

$$x_c = \frac{\rho_s - \rho_a}{\rho_c - \rho_a}$$

Where rs is the density of the sample, rc is the density of the crystals, and ra is the density of completely amorphous polymer.

VI.3.4. Tacticity

The arrangement of side-groups along a polymer chain significantly influences its properties, particularly the chain's flexibility, thereby affecting the polymer's melting point and the chains' ability to pack together. These variations impact both the strength and optical characteristics of the polymer. Three distinct arrangements have been identified: atactic polymers exhibit a random distribution of side-groups; isotactic polymers have all side-groups on one side of the chain; and syndiotactic polymers feature alternating side-groups (see

Figure VI.11). For instance, atactic polypropylene is mostly amorphous and weak. In contrast, syndiotactic polypropylene, a stereo-regular material, is crystalline, transparent, and rigid, while isotactic polypropylene also crystallizes and readily forms fibers. Similarly, in the case of polystyrene, the atactic variant is amorphous, whereas syndiotactic polystyrene is crystalline. Poly (methyl methacrylate), utilized as a glass substitute, is almost entirely amorphous.
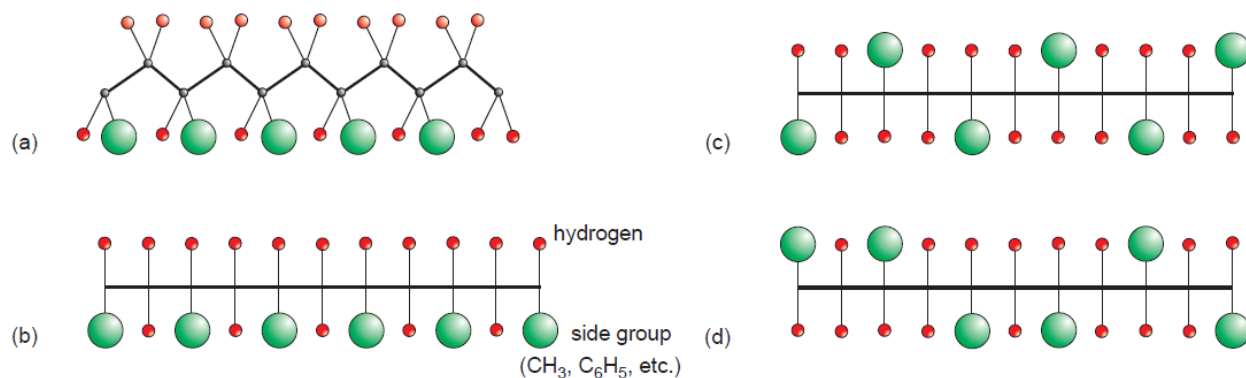

Figure VI.11: Polymer chains: (a) perspective view of an isotactic polymer chain; (b) projection of (a) from above; (c) a syndiotactic polymer chain depicted as in (b); (d) an atactic polymer chain depicted as in (b).

VI.3.5.   Cross-linking

The extent of cross-linking among chains induces significant changes in properties. Mild cross-links have a tendency to render materials softer, whereas extensive cross-linking transforms the material into a rigid resin. Examples like epoxy resins showcase a substantial degree of cross-linking, resulting in a hardened mass. Elastomeric properties, crucial for materials with elasticity, are closely tied to the process of cross-linking.

VI.3.6.   Copolymers

The properties of polymers undergo significant alterations when two different monomers are polymerized together to form copolymers. These copolymers can exhibit various structural arrangements, including an alternating sequence, a random distribution, extensive blocks of just one polymer or the other, or one

polymer attaching as branches to the main chain of the other (refer to Figure VI.12). The physical and chemical characteristics of these materials can be considered a combination of the properties of the two parent polymers. For instance, pure atactic polystyrene is transparent but brittle, while polybutadiene (synthetic rubber) is resilient yet soft. In contrast, high-impact polystyrene, a graft copolymer incorporating these two materials, possesses a combination of durability, strength, and transparency.
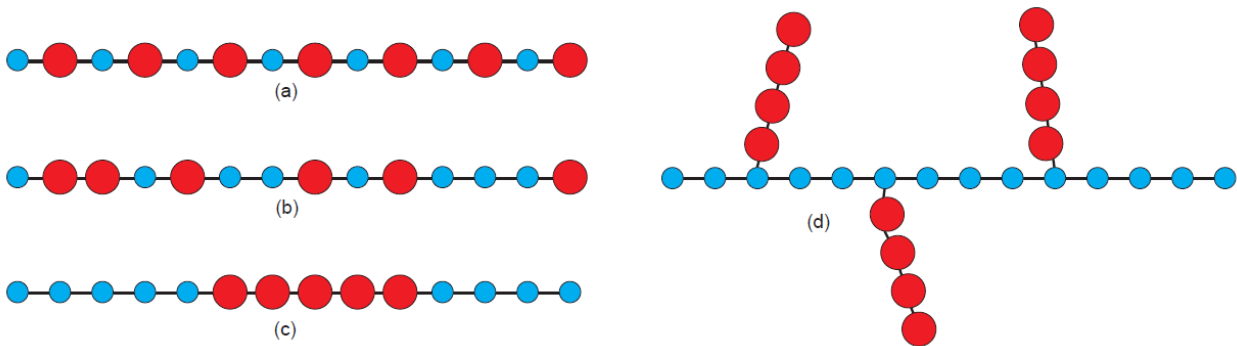

Figure VI.12: Schematic polymer geometry: (a) alternating copolymer; (b) random copolymer; (c) block copolymer; (d) graft copolymer.

VI.4. Production of polymers

Due to the critical influence of microstructures on polymer properties, the manufacturing of polymers requires highly skilled processes. The advancements in preparation methods play a significant role in the evolution of plastic properties. Polymer formation involves two primary mechanisms: step growth and chain growth. In step growth, chains can link together to create longer chains, while in chain growth, monomers are sequentially added to the growing chain's end, containing a reactive state, often a free radical—a highly chemically reactive molecule or fragment with an unpaired electron (Figure VI.13). Notably, step-growth mechanisms, such as the one observed in the formation of nylons, contribute to the development of certain polymers. Furthermore, linkages can occur in various ways, including head-to-tail (the most common), head-to-head, tail-to-tail, and random, adding complexity to the reaction.
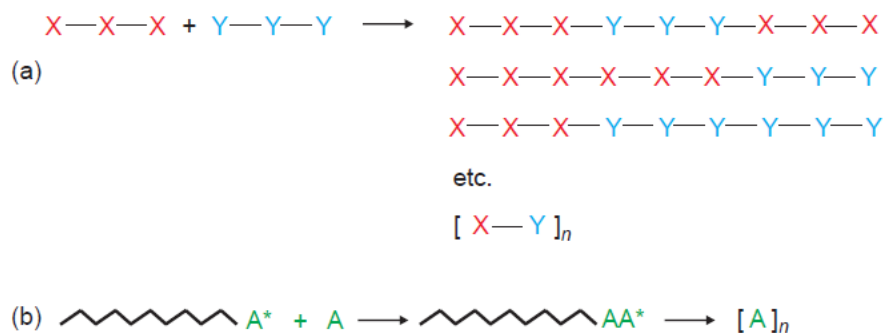
Figure VI.13: Polymerisation mechanisms: (a) in step growth, short chains link to give a variety of sequences; (b) in chain growth, new molecules add to one end of a growing chain. A represents a free radical or similar active center.

VI.4.1. Initiation, propagation and termination

Initiating the polymer formation process involves activating the initial monomers, a step known as initiation. This activation can be achieved through methods like applying heat or utilizing high-energy radiation, such as ultraviolet light. However, these processes, while effective, lack the reproducibility required for industrial production and can contribute to polymer degradation during regular usage. In industrial settings, initiation is achieved by mixing a diverse range of active molecules with the monomers.

The ongoing generation of polymer chains through the linkage of monomers, constituting the second stage of the reaction, is referred to as propagation. The mechanisms involved in propagation are intricate, and a complete understanding of all reaction steps is not universally attained for every reaction. Nonetheless, the propagation stage holds crucial significance in the production of specialized polymers, often necessitating the use of catalysts. In many instances, catalysts not only accelerate the reaction rate but also ensure a controlled addition of monomers to the growing polymer chain. This controlled approach implies that reacting molecules approach the growing chain in a specific direction. This controlled tacticity leads to the production of polymers with a uniform structure, exemplified by isotactic polystyrene. Catalysts such as

Ziegler-Natta and metallocene fall into this category and are employed to fabricate polymers with precisely controlled structures.

The growth of polymer chains inevitably needs to cease, a process facilitated by termination. Chain termination occurs through two distinct mechanisms. The first involves the straightforward meeting and merging of two growing chains. In such instances, the reactive ends of the chains, typically free radicals with unpaired electrons, unite as the free electrons form bonds connecting the chains (Figure VI.14a). The second mechanism, known as disproportionation, allows one growing chain to extract a hydrogen atom from another chain. This results in one chain terminating with a $-CH_3$ group, and the other forming a double bond (Figure VI.14b). Subsequent reactions at this double bond can extend the length of the chain. Additionally, the hydrogen can be extracted from the middle of a chain, terminating one chain with a $-CH_3$ group and generating a free radical within the chain's interior. This reactive region can serve as a center for new chain growth, leading to the formation of a branch (Figure VI.14c). This occurrence is prevalent in polyethylene polymerization, contributing to the highly branched structure of low-density (LD) polyethylene as described earlier. To produce much stronger, non-branched high-density (HD) polyethylene, alternative preparation methods must be employed.
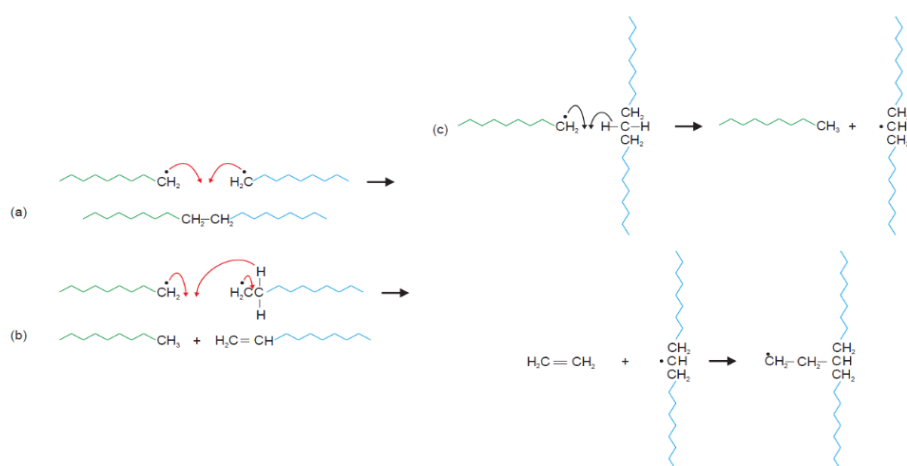

Figure VI.14: Chain termination: (a) two chains meeting; (b) disproportionation; (c) disproportionation leading to branching.

VI.4.2.   Metallocene catalysis

Metallocenes originate from the anion of cyclopentadiene, denoted as $(C_5H_5)^-$ in Figure VI.15a. These stable entities feature a delocalized orbital positioned both above and below the plane formed by the pentagon of carbon atoms. This arrangement facilitates the establishment of robust chemical bonds with metal cations. The initial metallocene under investigation, ferrocene, harbors Fe^{2+} sandwiched between the anions, as depicted in Figure VI.15b. Catalysts employed in current polymer production are derived from zirconocene, housing Zr^{4+} cations (Figure VI.15c). To achieve polymers with specific structures, the components surrounding the Zr^{4+} ion undergo meticulous modifications. Altering the cyclopentadiene anions induces changes in the monomer approach geometry to the cation.

Control over the point where the polymer chain elongates is achieved by substituting Clions with methyl (CH_3) groups, with the methyl group serving as the attachment point for successive monomer molecules. In the synthesis of polypropylene (Figure VI.15d), each cyclopentadiene group is replaced by a complex structure known as an indentyl group, consisting of a benzene ring linked to a cyclodiene. The indentyl groups are connected by a short chain of two $CH2$ groups. By aligning these groups in opposition (Figure VI.15e), incoming monomers are directed to a position conducive to the exclusive formation of isotactic polypropylene. Conversely, in molecules where bulky groups reside on the same side of the Zr^{4+} cation (Figure VI.15e,f), the monomer approach varies, resulting in the production of atactic polypropylene
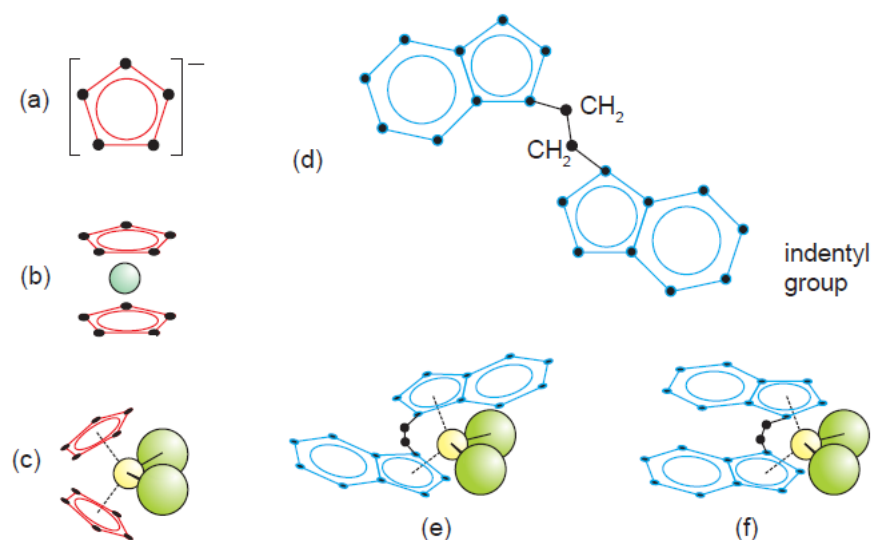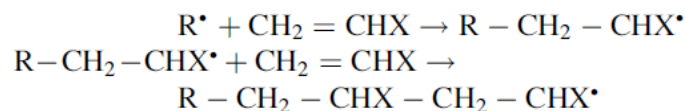
Figure VI.15: Metallocene catalysis: (a) carbon atom framework of $[C_5H_5]^-$; delocalised p molecular orbitals above and below the plane of the carbon atoms are represented by the circle; (b) ferrocene, in which Fe^{2+} is sandwiched between two $[C_5H_5]^-$ anions; (c) zirconocene, in which Zr^{4+} is bonded to two $[C_5H_5]^-$ anions and two Cl^- anions; (d) two identyl groups linked by two CH_2 groups; (e) molecular geometry required to produce isotactic polypropylene; (f) molecular geometry required to produce atactic polypropylene.

VI.4.3.   Free radical polymerisation

Free radical polymerization consolidates initiation and propagation into a single process. This technique is employed in the production of low-density branched polyethylene, poly (methyl methacrylate), and poly (vinyl acetate). Using ethene (ethylene) as an illustration, the gas undergoes pressurization to 100 atm. at 100 °C, and a small quantity of an unstable initiator molecule, typically an organic peroxide or azide, is introduced (Figure VI.16 a,b). These initiators decompose, generating highly reactive free radicals that attack double bonds, thereby initiating polymerization (Figure VI.16 c). The reaction satisfies the bonding requirements of the initial free radical while simultaneously generating a new free radical, which can further attack another ethene molecule, resulting in

continued chain growth (Figure VI.16 d,e). The reactions can be expressed as follows:

$$R^{\bullet} + CH_2 = CHX \rightarrow R - CH_2 - CHX^{\bullet}$$
$$R-CH_2-CHX^{\bullet} + CH_2 = CHX \rightarrow$$
$$R - CH_2 - CHX - CH_2 - CHX^{\bullet}$$

Here, R^* denotes an organic free radical. Free radical polymerization is possible with numerous ethene derivatives, though not all. The absence of constraints on the chain growth results in atactic polymers.
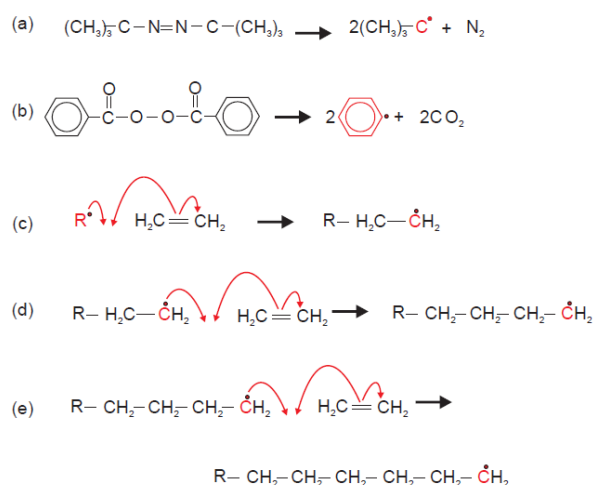

Figure VI.16: The generation of free radicals ($^{\bullet}$) by bond breaking: (a) an azide; (b) a peroxide. (c, d, e) Reactions of a free radical, R, with ethene.

VI.5. Elastomers

Elastomers exhibit rubber-like behavior, demonstrating the ability to stretch significantly beyond their original length. Upon release of applied force, they promptly revert to their initial size and shape. Classified as a subset of amorphous thermoplastics, elastomers are characterized by their dependence on the polymer's glass transition temperature, Tg. In contrast to conventional thermoplastics, which are rigid and brittle at room temperature due to a high glass transition temperature, elastomers possess a Tg below room temperature, rendering them soft and easily deformable at normal conditions. Consequently, cooling an elastomer well below its glass transition temperature results in

increased hardness and brittleness. For instance, immersing a rubber tube in liquid nitrogen causes it to become brittle, making it susceptible to fragmentation with a hammer blow.

In its natural state, the microstructure of an elastomer appears as a chaotic arrangement of intertwined and coiled polymer chains (Figure VI.17a). When subjected to stretching forces, these chains tend to partially align parallel to each other, as illustrated in Figure VI.17b. The stretched configuration is thermodynamically less stable than the coiled state, and the material reverts to its original coiled form once the deforming stress is removed. The greater entropy of the coiled state serves as the driving force for the material to return to this configuration. However, the crucial "snap-back" property of elastomers is not solely governed by entropy. This distinctive characteristic is achieved by introducing cross-links between some elastomer molecules using other molecules. As the elastomer is stretched, certain bonds in the cross-links undergo extension, and they promptly recoil when the tension is released.

The most widely recognized elastomer is natural rubber, which is composed of polyisoprene. Isoprene (Figure VI.18a) exists as a liquid at room temperature and readily undergoes polymerization to form the elastomer polyisoprene (Figure VI.18b). The polymerization process results in two primary geometrical isomers (molecules with identical formulas but distinct bond arrangements). Natural rubber represents the all-cis form of polyisoprene (Figure VI.18c), where the methyl (CH_3) groups and hydrogen (H) atoms are positioned on the same side of the carbon–carbon double bond. Another isomer, the all-trans form known as gutta-percha (Figure VI.18d), is also naturally occurring. It is harder in texture and finds applications in areas such as golf balls and dentistry.
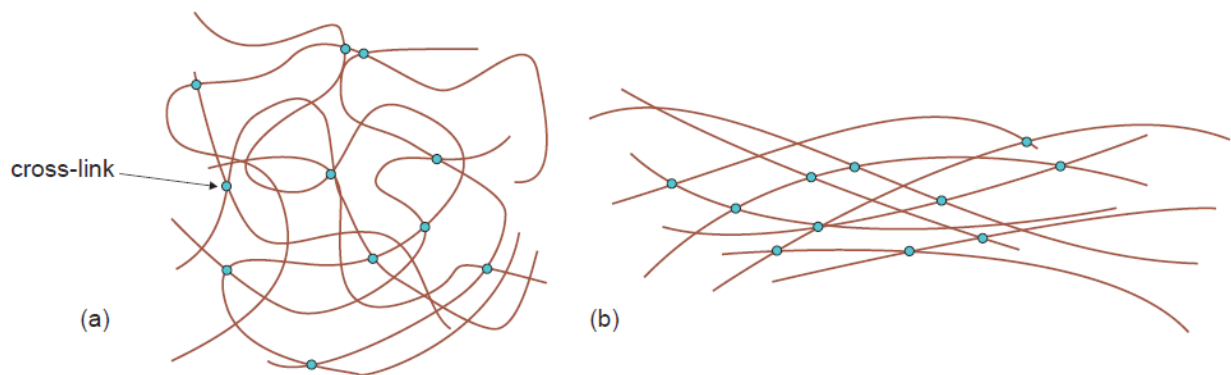
Figure VI.17: Elastomer (schematic) in (a) an unstretched, and (b) a stretched state.
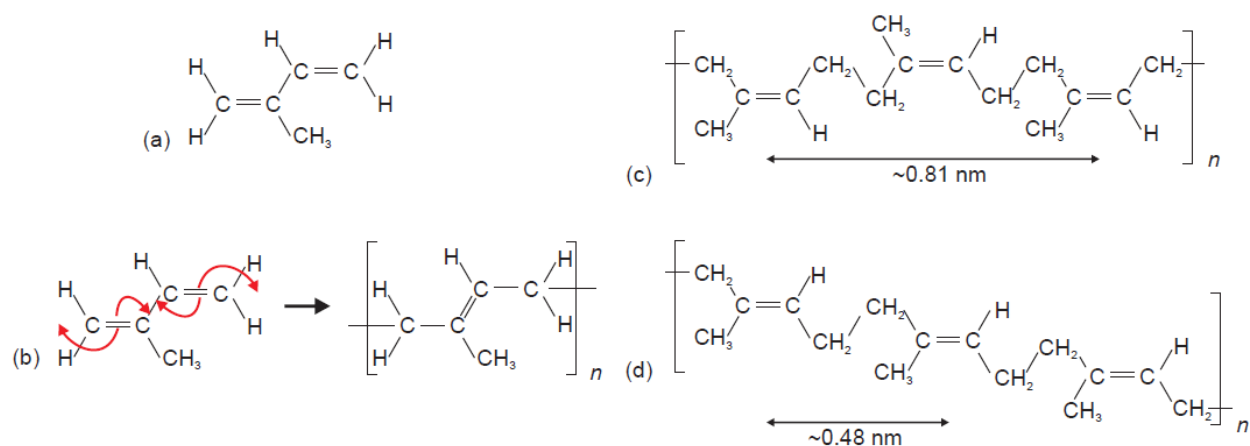

Figure VI.18: Rubber: (a) the structure of isoprene; (b) bond redistribution and polymerisation to form poly(isoprene); (c) natural rubber, all-cis-poly(isoprene); (d) gutta-percha, all-trans-poly(isoprene).

Rubber latex, a milky liquid extracted from rubber trees, constitutes a rubber-water suspension. It is present in various plants, such as dandelions. The addition of acetic acid can coagulate the rubber in latex, resulting in a soft and easily oxidizable substance known as crepe or gum rubber. In its unprocessed form, this rubber exhibits stickiness, akin to many amorphous thermoplastics above their glass transition temperature (Tg). It lacks the characteristic elastomer properties of snapping back when stretched.

In 1839, Goodyear discovered the process of cross-linking polyisoprene chains in natural rubber to create a functional elastomer. This method, known as vulcanization, involves heating natural rubber latex with sulfur. The result is a transformation of the initially sticky and runny natural material into a product that retains elastic properties while eliminating stickiness. The cross-linking process (refer to Figure VI.19) utilizes the remaining double bonds in the elastomer chains. Sulphur molecules open these bonds to form ties, making the polymer more rigid.

To achieve a soft rubber, approximately 1 or 2% of sulfur is added. However, excessive cross-linking can turn the polymer into a solid block. Hard rubbers, with up to 35% sulfur content, undergo extensive cross-linking, resembling thermosetting polymers like epoxy resins.

The discovery led to the production of a diverse family of artificial rubbers related to natural rubber. Early examples include buna rubber, obtained through the polymerization of butadiene in the presence of sodium (Na). Neoprene (refer to Figure VI.19a), a rubber resistant to organic solvents, is prepared from a chlorinated hydrocarbon precursor. Another widely used rubber is nitrile rubber (refer to Figure VI.19b), a copolymer of butadiene ($(CH_2=CH-CH=CH_2)$) and propenenitrile ($(CH_2=CH-CN)$), featuring a nitrile ($cyanide, -CN$) group.

-CH₂-C(CH₃)=CH-CH₂CH₂-C(CH₃)=CH-CH₂CH₂-C(CH₃)=CH-CH₂ + *n* S ⟶

-CH₂-C(CH₃)-CH-CH₂CH₂-C(CH₃)-CH-CH₂-CH₂-C(CH₃)=CH-CH₂

-CH₂-C(CH₃)-CH-CH₂CH₂-C(CH₃)=CH-CH₂CH₂-C(CH₃)-CH-CH₂

-CH₂-C(CH₃)-CH-CH₂CH₂-C(CH₃)=CH-CH₂CH₂-C(CH₃)-CH-CH₂

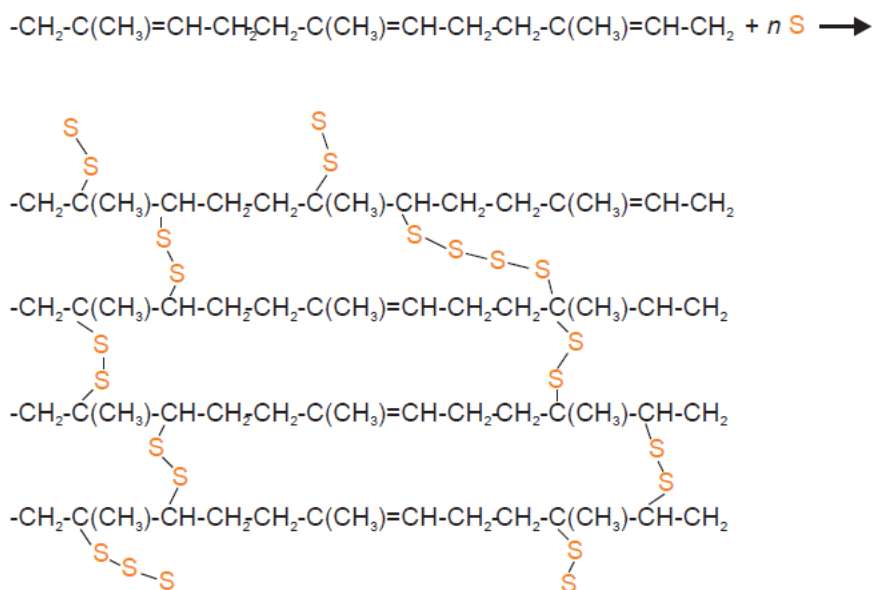-CH₂-C(CH₃)-CH-CH₂CH₂-C(CH₃)=CH-CH₂CH₂-C(CH₃)-CH-CH₂

Figure VI.19: The formation of sulphur cross-links between rubber molecules, produced during vulcanisation.

VI.6.   The principal properties of polymers

Polymers primarily consist of carbon and hydrogen, and a key characteristic of this category of materials is their low-density solid nature. This is attributed to the loose packing of polymer chains, preventing close proximity. The crystalline regions within polymers contribute to increased overall density.

Various polymer properties are influenced by functional groups present on the chains. Nylon fibers derive strength from hydrogen bonding between iNH and O=Ck. This bonding allows water absorption, contributing to the comfort of clothing made from these materials. The NH group in polymers can accumulate charge from water, leading to electrostatic charge buildup on carpets and clothing.

Polymers exhibit diverse properties that can be modified through processing and additives. Introducing a few cross-links into a thermoplastic elastomer transforms it from a sticky substance to a useful rubber. While inherently

insulating, doping can turn polymers into efficient electronic and ionic conductors, enabling their use in lightweight batteries.

The behavior of polymers under stress varies based on their structure and microstructure. Thermoplastic polymers are brittle at low temperatures and become easily deformable and plastic at higher temperatures due to unlinked polymer chains. Crystalline regions in thermoplastics enhance strength, while cross-linking in thermosetting polymers prevents molecular movement, resulting in mechanically robust and chemically stable solids.

A notable property of polymers lies in their chemical stability, leading to slow degradation. However, the persistence of polymers in the environment, especially in oceans, poses a pollution problem. The difficulty in degrading polymers is attributed to the strong carbon–carbon backbone and resilient carbon–hydrogen bonds. To enhance degradability, weak links, such as double bonds, oxygen atoms, or hydroxyl/acid groups, can be introduced into the polymer chains. This deliberate incorporation facilitates water penetration and bacterial attack, promoting degradation. The challenge lies in finding a balance to address environmental concerns while maintaining the desired properties of polymers.

Exercise:

1. Polystyrene is an example of:

    a. An addition polymer.
    b. A condensation polymer.
    c. An elastomer.

2. Nylons are:

    a. Polyamides.
    b. Polyesters.
    c. Polycarbonates.

Chapter VII : Composite materials

VII.1.   Introduction

These kinds of materials are solids composed of multiple materials, engineered to possess superior properties compared to the individual components. Nature is abundant with examples of composites: wood combines strong, flexible cellulose with rigid lignin, and bone merges strong, soft collagen (a protein) with hard, brittle apatite (a ceramic).

In the realm of human-made materials, composites are extensively utilized in advanced engineering, from aircraft to high-tech leisure products like skis and sails. One of the earliest uses of a composite material was in the Macintosh raincoat, which featured natural rubber sandwiched between two layers of woven cotton.

Artificial composites can be categorized into three main types based on the primary material of the composite, known as the matrix: polymers, metals, or ceramics. Often, composites mix materials from two different categories, such as glass fiber-reinforced plastics. However, the most commonly used composite, concrete, is a ceramic–ceramic composite.

Below, the key classes of artificial composites are detailed, with their mechanical properties.

VII.2.   Fiber-reinforced plastics

The primary polymers used as matrices in polymer composites are thermosetting resins, particularly polyester and epoxy resins. Polyester resins are relatively inexpensive but tend to shrink during curing and absorb water. In contrast, epoxy resins are more expensive, but they do not shrink during curing and are quite resistant to water penetration. Generally, any highly cross-linked polymer can serve as a potential matrix. These resins are reinforced by incorporating materials such as fiberglass, carbon fiber, or strong polymer fibers like Kevlar, an aramid fiber.

Fibers alone are typically brittle and, despite having good tensile strength, cannot easily sustain compression. Thus, the matrix's role is to hold the fibers together in the desired orientation. The fibers, in turn, provide added strength. The resultant strength of the composite depends on the type of fiber used and various geometric factors, including the amount of fiber added, the length and orientation of the fibers (Figure VII.1), and the bonding between the matrix and the fiber inserts. Composites exhibit strength in the direction of fiber alignment and are weaker perpendicular to this direction. To address this, the orientation of successive layers of fibers is often altered to form a laminate (Figure VII.2).
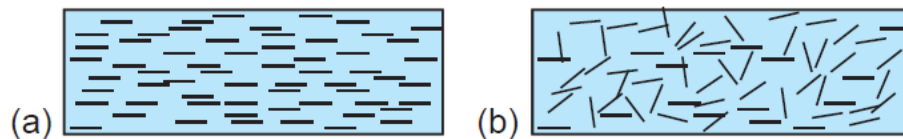

Figure VII.1: a- composite reinforced with aligned fibers. b- composite reinforced with randomly oriented fibers.
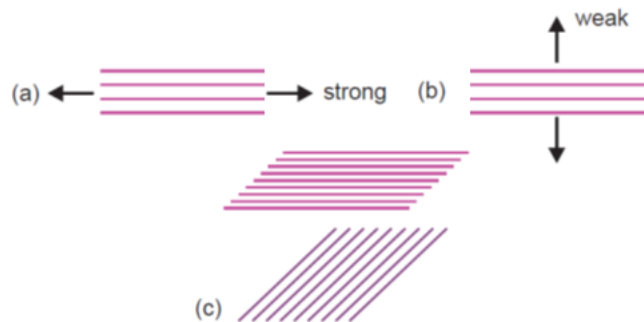

Figure VII.2: Reinforcing fibers are typically strong under tension (a) but weak when exposed to transverse forces (b). Laminates with fibers oriented in various directions help mitigate this weakness (c).

VII.3.   Metal-matrix composites

Metals are often reinforced with continuous fibers to enhance their strength. These fibers can be ceramic, such as silicon carbide or alumina, or metallic, like boron or tungsten. However, due to the difficulty in fabricating fibers from these materials, composites are typically made using small particles of a hard material

like alumina or silicon carbide unless exceptional performance is necessary. These ceramics are mixed with molten alloy and then shaped into the desired forms. Cemented carbide materials, commonly used as cutting tools for machining steel, are among the most prevalent metal-particle composites. The first cemented carbide was made from a cobalt metal matrix with hard tungsten carbide particles. This initial combination proved superior, and despite numerous attempts to find better metal-metal carbide combinations, the cobalt-tungsten carbide composite remains the most effective for most applications.

VII.4.   Ceramic-matrix composites

Ceramic-matrix composites are used to address the inherent brittleness of ceramics by incorporating fibers or particles as reinforcement. Materials such as silicon carbide and alumina are commonly employed for this purpose. These reinforcements enhance toughness by deflecting or bridging cracks in the ceramic matrix. Naturally occurring ceramic-ceramic composites include granite and marble. While glass in composites is typically associated with its strengthening role as fibers, laminated glass is another widely used composite. Laminated glass consists of a thin plastic film sandwiched between two or more sheets of glass, which prevents the glass from splintering on impact. This type of glass is extensively used as bulletproof glass.

VII.5.   Cement and concrete

Concrete is a composite material composed of cement paste and aggregate, which is a coarse, stony substance. The cement paste itself is a blend of cement and water. When the aggregate used is sand, the resulting mixture of cement, water, and sand is known as mortar.

Early forms of cement, primarily consisting of calcium hydroxide, partially converted to calcium carbonate, date back to before Roman times. This material was produced from limestone (an impure form of calcium carbonate), which was heated or burned to create quicklime or burnt lime (calcium oxide).

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Quicklime reacts with water in a process called slaking, which releases a significant amount of heat and produces slaked lime (calcium hydroxide).

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$
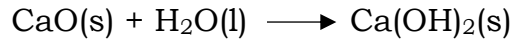
Slaked lime was combined with water to form a paste, which was used to bind sand or stone. This paste gradually reacted with carbon dioxide in the air, converting back into calcium carbonate.

$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$
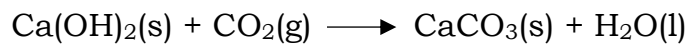
The Romans enhanced the process by adding volcanic ash to the limestone, creating a more durable cement that remains intact to this day.

VII.5.1.   Example of cement: Portland cement

Portland cement was first formulated by Joseph Aspdin of Leeds, who patented it in 1824. He named it Portland cement because it resembled the expensive Portland Stone to his eye. Various manufacturers worked to improve the material, but the version now known as Portland cement was developed by Joseph Aspdin's son, William, in the 1840s. This cement is made from approximately 80% limestone and 20% clay. It was widely adopted due to its superior qualities compared to older quicklime-based materials, particularly its ability to harden in damp conditions. This property was especially valuable during the extensive tunnel construction for projects like the London Underground system.

To produce cement powder, the raw materials are ground with water to form a slurry, which is then heated in a kiln at gradually increasing temperatures. This process initially drives off water and then decomposes the calcium carbonate.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

As the temperature rises, additional reactions occur, causing the reaction products to partially melt and sinter, forming clinker. In the final manufacturing

stage, the cooled clinker is ground, and approximately 2–5% gypsum $(CaSO_4.2H_2O)$ is added to create cement powder.

Portland cement powder consists of five primary constituents, which are complex minerals identified by their chemical names, mineral names, and shorthand notation (see Table VII.1). Ordinary cement powder also contains trace amounts of other impurities that can significantly influence the ultimate strength and durability of concrete.

Table VII.1: constituents of Portland cement.

Chemical name	Mineral name	Chemical formula	Shorthand notation	Typical composition/wt %
Tricalcium silicate	Alite	Ca_3SiO_5	C_3S	40–65
Dicalcium silicate	Belite	Ca_2SiO_4	C_2S	10–20
Tricalcium aluminate		$Ca_3Al_2O_6$	C_3A	10
Tetracalcium aluminoferrite		$Ca_4Al_2Fe_2O_{10}$	C_4AF	10
Calcium sulphate dihydrate	Gypsum	$CaSO_4.2H_2O$	CSH_2	2–5

Exercise:

1. Ceramic matrix composites are designed to overcome:
   a. The weight of ceramics.
   b. The brittle nature of ceramics.
   c. The inertness of ceramics.

2. The main source of heat when Portland cement hardens is due to the reaction of:
   a. Tricalcium silicate.
   b. Dicalcium silicate.
   c. Tricalcium aluminate.

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