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Non Metallic Materials

Course Handbook

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PREFACE

In modern mechanical engineering, materials are no longer limited to metals. The increasing demand for lightweight, durable, and cost-effective solutions has placed non-metallic materials such as polymers, composites, ceramics, and glasses at the forefront of engineering design and innovation.

This course is designed for LMD Bachelor's students specializing in Mechanical Construction, aiming to provide a solid foundation in the classification, structure, properties, and applications of non-metallic materials. These materials, though often overlooked in traditional curricula, are essential in industries ranging from aerospace and automotive to biomedical and civil engineering.

The course explores the fundamental differences between metallic and non-metallic materials, focusing on:

- ✓ the molecular and structural characteristics of polymers,
- ✓ the thermal and mechanical resistance of ceramics and glasses,
- ✓ and the tailored performance of composite materials,
- ✓ all while considering processing methods, standards, and design implications.

Understanding these materials enables future engineers to make informed decisions in material selection, manufacturing processes, and product development. By the end of the course, students will be equipped not only to recognize the potential of non-metallic materials in mechanical design but also to contribute meaningfully to innovation and sustainability in engineering applications.

This manual is structured to be both didactic and practical and aligns with the LMD system's goals of competency-based learning. It serves as a reference for lectures, exercises, and project work, encouraging the development of analytical and critical thinking in material science.

Chapter I

Overview of Plastics

I.1 Introduction

The functional properties of materials largely depend on their physicochemical characteristics, which, in turn, are governed by the nature of the atomic bonds linking their constituent atoms. Based on these bonding types, materials are classified into the main families of materials. Each class exhibits specific properties that directly influence their mechanical, thermal, electrical, and chemical behavior, thereby defining their fields of application.

I.2 Classification of Materials

There are four major classes of materials:

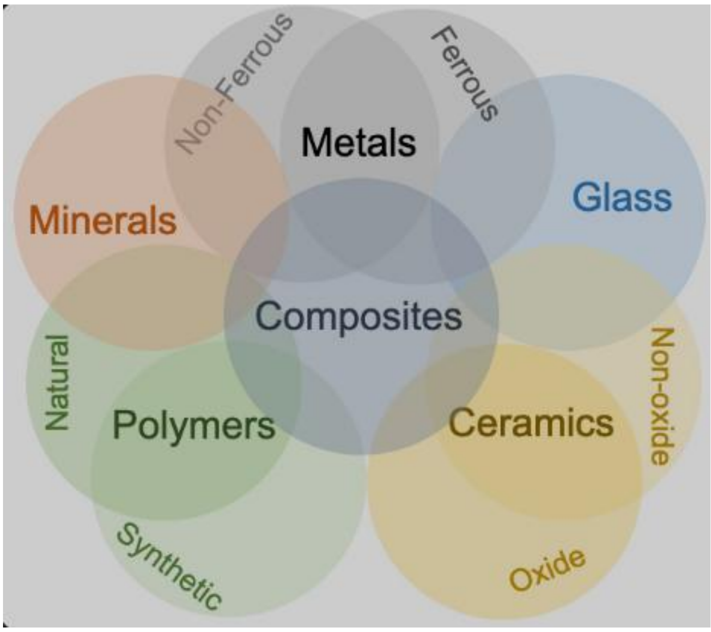


Figure 1.8:The four main families of materials.

I.2.1 Metallic Materials

These include pure metals, mixtures, or alloys, all of which are primarily characterized by metallic bonding.

I.2.2 Organic Materials

Organic materials are derived from biological sources and are mainly characterized by weak and covalent bonds.

I.2.3 Mineral Materials

Mineral materials include ceramics, glass, rocks, and oxides, and are characterized by ionic and/or covalent bonding.

I.2.4 Composite Materials

Depending on the nature and structure of their components, the properties of composite materials can vary widely. In most cases, their properties are intermediate between those of the individual constituent materials.

I.3. Structures and properties

Organic materials, or polymers, represent one of the three major classes of engineering materials, alongside metals and ceramics/glasses.

Polymers occur naturally in various forms such as wood, rubber, cotton, leather, silk, proteins, enzymes, starches, and cellulose. Synthetic polymers, in contrast, are primarily derived from petroleum. Their use has increased exponentially, particularly following World War II. This growth is largely due to their low production cost and valuable properties for example, the combination of transparency, flexibility, and high elongation at break.

Commonly referred to as plastics, polymers are now inseparable from our daily environment. They are used in every aspect of life from the most visible to the most discreet applications, from everyday household items to highly technical products, including packaging, hygiene items, and even food containers.

What Is a Polymer?

The word polymer comes from the Greek “polus” (many) and “meros” (unit or part), and refers to any material formed by the repetition of a large number (n) of small molecules called monomers, which are connected via primary (covalent) bonds. A monomer is a small, reactive molecule often unsaturated, cyclic, or containing functional groups at its ends that serves as the building block for polymer chains. The chemical process that links monomers into polymers is called polymerization, and the resulting long molecule is called a macromolecule.

Polymers are organic materials, meaning their molecular backbone is made up of carbon atoms. Each carbon atom has four valence electrons that can form covalent bonds with other carbon atoms or with other elements. Two carbon atoms can even share up to three bonds, allowing for a wide range of structural configurations.

The most common elements in polymer chains and their typical valence numbers are:

H, F, Cl, Br, I → 1 valence electron
O, S → 2 valence electrons
N → 3 valence electrons
C, Si → 4 valence electrons

A polymer is thus composed of many repeating structural units (monomers), which can number from a few hundred to several million in a single chain. These chains may be linear, branched, or cross-linked into a network.

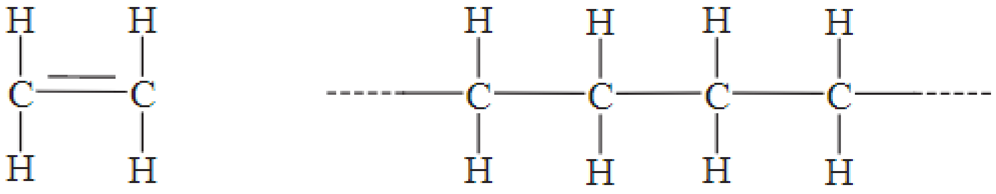
Covalent bonds hold the atoms together within each polymer chain. Secondary forces (such as Van der Waals interactions) bind the chains to each other, giving rise to the bulk polymer material. Polymers made from two or more different monomers are called copolymers.

Example: Polyethylene

A simple example is polyethylene, derived from the monomer ethylene (C_2H_4). The ethylene molecule contains a double bond between the two carbon atoms and single bonds with hydrogen atoms. When exposed to heat or a catalyst, the double bond "opens", initiating a polymerization reaction that forms long chains:

$$(C_2H_4)n \rightarrow –[CH_2–CH_2]n$$

The resulting macromolecule consists of thousands to millions of repeating $–CH_2–CH_2–$ units. The C–C and C–H bonds in the chain are strong covalent bonds, responsible for the stability of the chain itself. The interactions between chains are much weaker, typically Van der Waals forces, which influence the mechanical and thermal properties of the material.



(a) **(b)**

Figure I.1 : Monomer C_2H_4 and Macromolecular Chain $(C_2H_4)n$

The spatial arrangement of monomers relative to one another is referred to as the stereoregularity or stereochemistry of the chain.

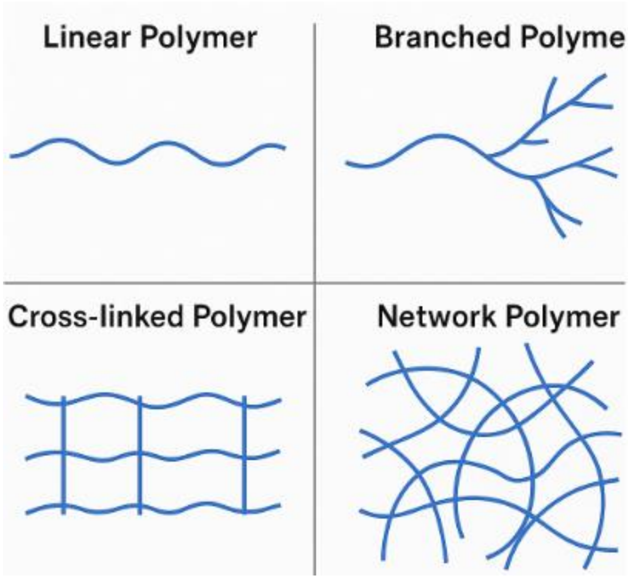


Figure I.2 : Different type of polymer

I.4 Macromolecular scale

I.4.1 Amorphous Polymers and Crystallized Polymers

- **Amorphous Structure**

Amorphous polymers are characterized by a disordered molecular arrangement, where the polymer chains are randomly entangled without any long-range order. This irregular structure gives them transparency, flexibility, and gradual softening over a temperature range rather than a sharp melting point.

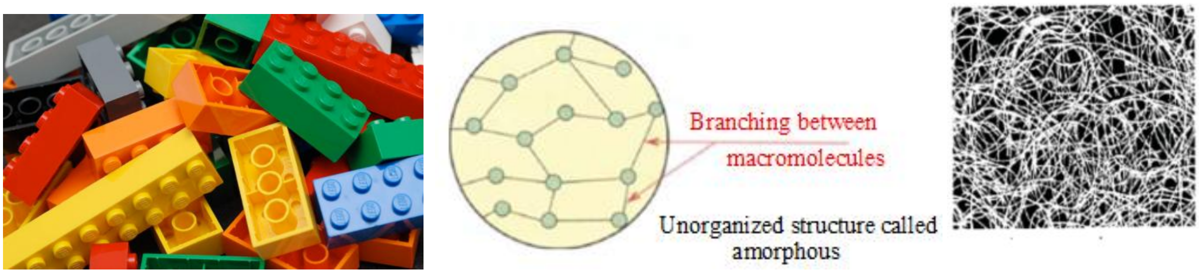


Figure. I.3: Part made of amorphous Acrylonitrile Butadiene Styrene (ABS) polymethyl methacrylate.

- **Semi-Crystalline Structure**

Semi-crystalline polymers have regions of ordered (crystalline) structure interspersed with disordered (amorphous) regions. This combination gives them distinct properties such as higher mechanical strength, a well-defined melting point, and greater chemical resistance compared to fully amorphous polymers.

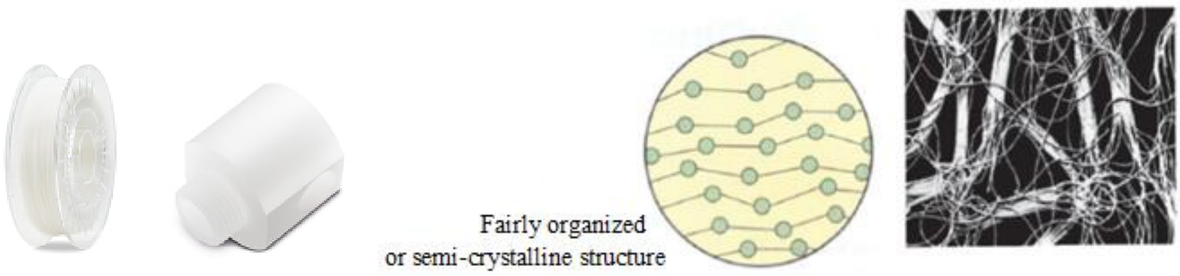


Figure. I.4: semi-crystalline polyamide (PA) part typically

I.5 Processing and manufacturing techniques

The transformation of polymers into final products involves various processing and manufacturing techniques, depending on the nature of the polymer (thermoplastic, thermoset, elastomer) and the desired shape or performance.

I.6 Applications and Processing of Polymers

Polymers are widely used across almost every sector of modern life. Grocery bags, soda and water bottles, textile fibers, mobile phones, computers, food packaging, automotive parts, and toys all contain polymers. Their versatility and range of properties make them essential in numerous industries. Here are the main fields of application:

I.6.1 Medicine

Polymers play a crucial role in the field of medicine. Many biomaterials such as artificial heart valves and blood vessel grafts are manufactured from polymers like Dacron, Teflon, and polyurethane. These materials are selected for their biocompatibility, flexibility, and durability, allowing them to perform vital functions inside the human body without causing rejection or severe reactions.

- **Examples**:

- Artificial arteries
- Heart valve replacements
- Surgical sutures

I.6.2 Consumer Products

In consumer goods, polymers are valued for being lightweight, durable, and cost-effective compared to traditional materials like glass or metal. They are widely used for manufacturing plastic containers of various shapes and sizes, clothing fibers, floor coverings, trash bags, and packaging materials.

- **Examples**:

- Plastic water bottles
- Food wrapping films
- Synthetic clothing (e.g., polyester, nylon)

I.3.2 Industry

In industrial applications, polymers provide mechanical strength, chemical resistance, and design flexibility. They are used in producing automotive parts, fighter jet windshields, pipes, storage tanks, insulation materials, adhesives, composite matrices, and elastomers. Their ability to replace heavier and often more expensive materials makes them vital for improving efficiency and reducing costs.

- **Examples**:

- Car bumpers and dashboards
- Aircraft canopies made from polycarbonate
- Industrial piping systems

I.6.3 Sports and Recreation

Polymers are extensively used in the sports industry for manufacturing playground equipment, balls, golf clubs, swimming pools, and protective helmets. They offer impact resistance, lightweight properties, and weather resistance, ensuring both performance and safety.

- **Examples**:

- Football helmets made from polycarbonate
- Tennis balls with a polymer core
- Fiberglass golf club shafts

I.7 Standardization and classifications

I.7.1 Standardization

The names of polymers are generally derived from the name of the monomer by adding the prefix "poly". If the monomer name consists of multiple words, it is placed in parentheses and preceded by "poly".

- **Example:** Poly(vinyl chloride)

For copolymers, a special suffix (unifixe) is used to describe the known arrangement of the repeating units. Copolymers are typically identified with terms such as "alternating copolymer," etc.

- **Example:** Poly[styrene-co-(methyl methacrylate)]

I.7.2 Classification

Polymers can be classified in several ways, depending on their properties, origins, and molecular structures:

a) Based on Origin

- **Natural Polymers:**
  Found in nature (e.g., cellulose, natural rubber, proteins).
- **Synthetic Polymers:**
  Man-made in laboratories (e.g., polystyrene, nylon, polyethylene).

b) Based on Structure

- **Linear Polymers:**
  Long straight chains (e.g., high-density polyethylene - HDPE).
- **Branched Polymers:**
  Chains with side-branches (e.g., low-density polyethylene - LDPE).
- **Cross-linked Polymers:**
  Three-dimensional networks (e.g., vulcanized rubber).

c) Based on Polymerization Type

- **Addition Polymers:**
  Made by linking monomers without any by-product (e.g., polypropylene).
- **Condensation Polymers:**
  Formed with by-products like water (e.g., nylon, polyester).

d) Based on Thermal Behavior

- **Thermoplastics:**
  Soften on heating and harden on cooling (e.g., polyethylene, PVC).
- **Thermosetting Polymers:**
  Harden permanently after heating (e.g., Bakelite, epoxy resins).

e) Based on Mechanical Properties

- **Elastomers:**
  Highly elastic (e.g., rubber).
- **Fibers:**
  Strong, thread-like (e.g., Kevlar).
- **Plastics:**
  Malleable and moldable (e.g., polystyrene).

Chapter II

Introduction to Polymeric Materials

II.1.1Introduction

Polymeric materials are essential in modern industry and everyday life, owing to their remarkable versatility, light weight, and customizable properties. Whether natural or synthetic, polymers form the basis of a wide range of products, from simple packaging films to advanced components used in aerospace and biomedical engineering. Understanding polymeric materials requires a thorough examination of their nature and structure, starting with the formation of macromolecular chains and the distinction between thermoplastics and thermosetting polymers. Their behavior can vary significantly, depending on whether they are amorphous or semi-crystalline, and whether they exhibit elastomeric characteristics. This chapter explores the fundamental properties of polymeric materials, including their mechanical, physical, and thermomechanical behaviors. We will also analyze how polymers perform under long-term aging, their combustion resistance, and the critical parameters affecting their processing techniques. Finally, an overview of polymerization methods by addition or condensation will provide a deeper understanding of how polymers are synthesized and how their structures influence their end-use properties.

II.2 Nature and Structure of Polymeric Materials

Polymers are primarily used in the production of polymeric materials, meaning any useful matter, whether of natural or synthetic origin, processed by humans and transformed to create objects (commonly referred to as "plastic objects" or simply "plastics") that provide specific functional properties.

The base polymer is often combined with additives and fillers that modify its physicochemical properties, thus adjusting the performance of the final plastic material. Polymers can come from natural sources (plant or animal origin) or be synthetically produced through the polymerization of monomers. Both natural and synthetic polymers can also undergo further chemical modifications to meet particular technical specifications. Specifically, an artificial polymer refers to a chemically modified natural polymer.

There is often confusion between the terms monomer unit and repeating unit:

The degree of polymerization is strictly defined as the number of monomer units within a macromolecule.

It is therefore essential to distinguish between the two:

- ✓ As its name suggests, the repeating unit is the structure that repeats along the polymer chain and primarily characterizes it.
- ✓ It can originate from a single monomer or from multiple monomers.

In the first case, monomer unit and repeating unit are identical.

In the second case, defining a repeating unit is more complex or even impossible in some structures.

The simplest situation occurs when different monomer units alternate along the chain: the repeating unit is then composed of the succession of two different monomers. Clear examples (to be added below) help illustrate the identification of monomers, repeating units, and monomer units without ambiguity.

II.3 Macromolecular Chains, Thermoplastics, and Thermosetting Polymers

II.3.1 Macromolecular Chains

Polymers are composed of extremely long chains of repeating units known as macromolecules. These macromolecular chains are formed by the chemical linking of thousands or even millions of small molecules called monomers.

The physical and mechanical properties of a polymer largely depend on:

- The length of the macromolecular chains (degree of polymerization),
- The type of bonding (covalent, van der Waals, hydrogen bonds),
- The degree of branching, cross-linking, or entanglement between chains.

Long, flexible chains tend to result in soft and ductile materials, while highly cross-linked chains lead to rigid and brittle structures.

II.3.2 Thermoplastics

Thermoplastics are polymers that become soft or moldable upon heating and harden again when cooled a process that is reversible and can be repeated multiple times. Their chains are either linear or slightly branched and are held together by weak intermolecular forces (such as van der Waals interactions), allowing them to flow under heat and pressure.

Key characteristics:

- ✓ Recyclable and reprocessable,
- ✓ Good flexibility and impact resistance,
- ✓ Sensitive to temperature changes.

Examples:

Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Poly(methyl methacrylate) (PMMA).

II.3.3 Thermosetting Polymers

Thermosets are polymers that undergo a chemical change during their initial processing, creating strong, irreversible covalent cross-links between chains. Once cured or hardened, they cannot be remelted or reshaped. Heating a thermoset after curing usually leads to decomposition rather than melting.

Key characteristics:

- ✓ High mechanical strength and thermal stability,
- ✓ Excellent chemical resistance,
- ✓ Brittle behavior at high degrees of cross-linking.

Examples:

Epoxy resins, Phenolic resins (Bakelite), Polyurethanes, Melamine-formaldehyde.

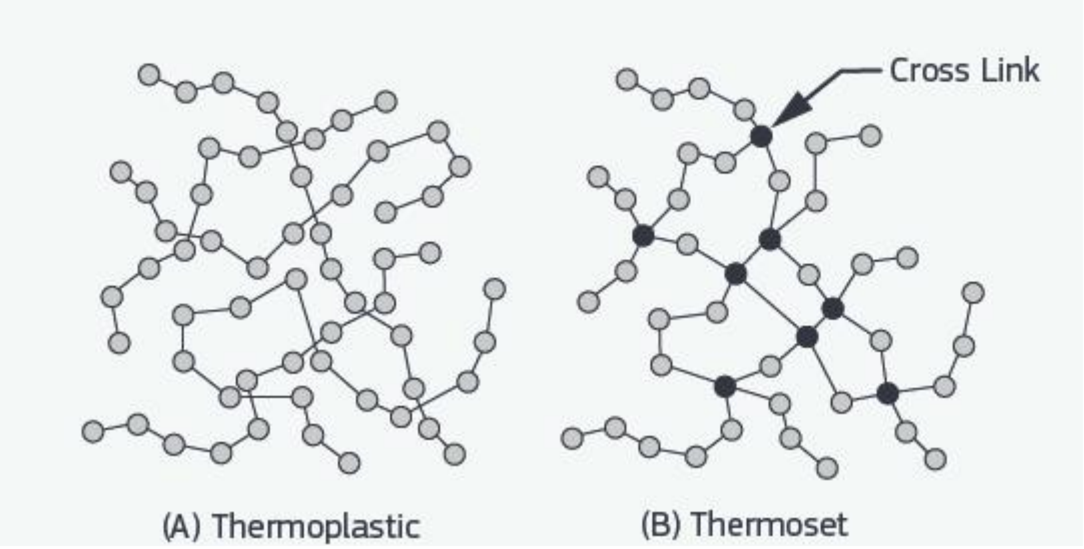


Figure. II.1: representation of (a) thermoplastic (b) thermosetting

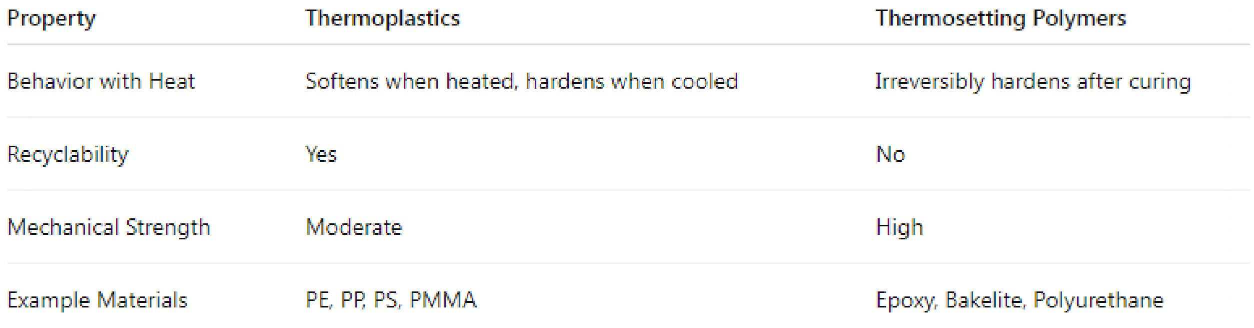
II.3.4 Elastomers

Elastomers are polymers characterized by their highly elastic properties, achieved through cross-linking processes. They can undergo very large deformations before rupture and have the ability to return to their original shape once the applied stress is removed. Commonly, the term "rubber" is used synonymously with elastomer.

Historically, natural rubber derived from the latex of Hevea trees native to the Amazon — was the only known elastomer. Modern manufacturing methods have since expanded the range of available elastomeric materials through the addition of additives such as accelerators, UV stabilizers, and oxygen inhibitors, and by combining elastomers with metals, textiles, and other plastics. Today, elastomers fall into three major categories, each encompassing a wide variety of products with diverse properties.

Elastomers exhibit distinctive characteristics, including exceptional elasticity, excellent sealing capabilities, and strong damping performance. While their primary use remains in the production of tires, elastomers are also widely employed in the form of seals, hoses, membranes, and vibration-damping devices across various sectors such as automotive, industrial manufacturing, aerospace, and medical fields. Unlike traditional plastics, elastomers are valued for their flexibility and resilience under extreme mechanical stresses.

Table II.1 property of thermoplastics and thermosetting



Property	Thermoplastics	Thermosetting Polymers
Behavior with Heat	Softens when heated, hardens when cooled	Irreversibly hardens after curing
Recyclability	Yes	No
Mechanical Strength	Moderate	High
Example Materials	PE, PP, PS, PMMA	Epoxy, Bakelite, Polyurethane

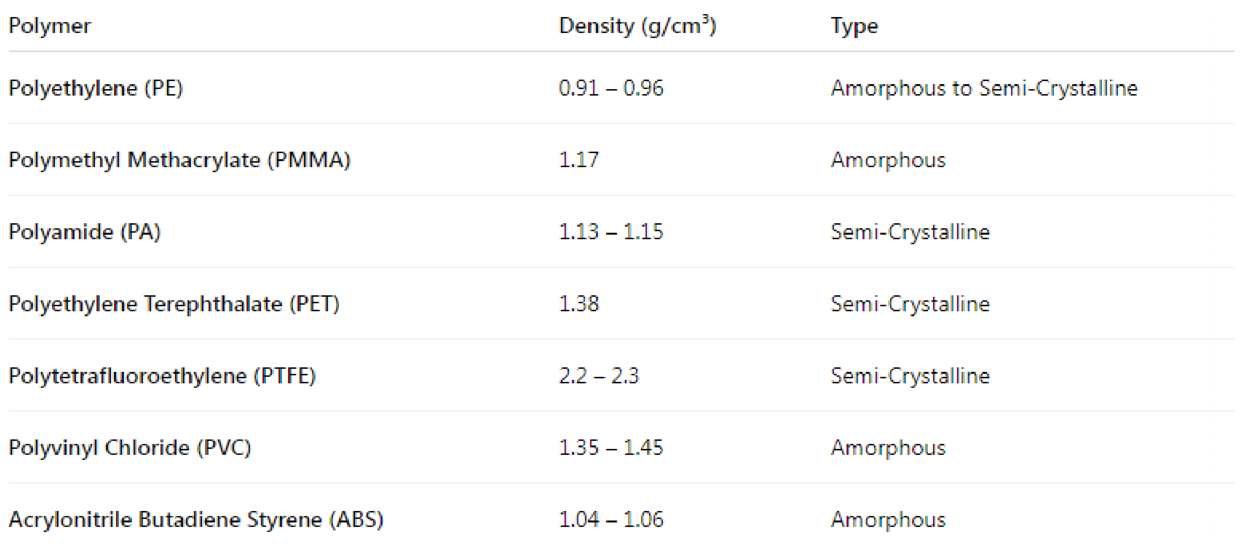
II.4 Polymer properties

The properties of polymer materials are much more sensitive than metals to external influences such as temperature, hardness, applied stress intensity, UV radiation, and chemical agents. The strength characteristics may differ by only one order of magnitude. In addition to specific material parameters (molar mass, branching rate, chain mobility, crosslinking rate, etc.), external conditions (humidity, chemical agents, temperature, loading rate, type, and intensity of applied stresses) also play a significant role.

II.4.1 Physical properties

The density of polymers refers to the mass per unit volume of a material. It is expressed in kg/m^3 or g/cm^3. Polymers generally have a lower density compared to metals and ceramics. The density varies depending on the polymer's structure: amorphous polymers typically have a lower density compared to semi-crystalline polymers.

Table II.2: Summarizing the density of different polymers**:**



Polymer	Density (g/cm³)	Type
Polyethylene (PE)	0.91 – 0.96	Amorphous to Semi-Crystalline
Polymethyl Methacrylate (PMMA)	1.17	Amorphous
Polyamide (PA)	1.13 – 1.15	Semi-Crystalline
Polyethylene Terephthalate (PET)	1.38	Semi-Crystalline
Polytetrafluoroethylene (PTFE)	2.2 – 2.3	Semi-Crystalline
Polyvinyl Chloride (PVC)	1.35 – 1.45	Amorphous
Acrylonitrile Butadiene Styrene (ABS)	1.04 – 1.06	Amorphous

II.4.2 Thermal Properties

Thermal properties of polymers play a crucial role in their performance and selection for different applications. These properties determine how polymers behave under varying temperature conditions, influencing their processing, stability, and end-use performance.

The Glass Transition Temperature (Tg) and Melting Temperature (Tm) are two fundamental temperatures required in the study of polymer materials.

The Glass Transition Temperature (Tg) is particularly important for amorphous polymers, especially amorphous thermoplastics, where no significant cohesive forces exist other than molecular entanglement.

The characteristic temperatures of a single polymer material can be classified as follows:

- Glass Transition Temperature (Tg) < Crystallization Temperature < Melting Temperature (Tm) < Thermal Decomposition Temperature**.**

Depending on the temperature to which it is exposed, a polymer material can exhibit different mechanical behaviors. This can occur even for semi-crystalline thermoplastics within a narrow temperature range.

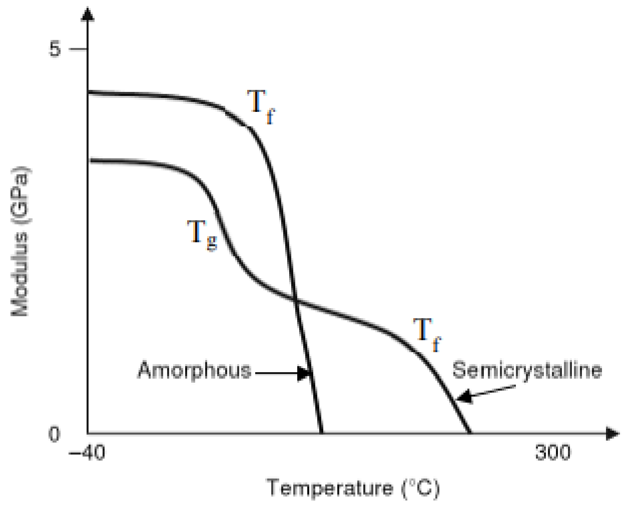


Figure II.2 : Variation of the Elastic Modulus as a Function of Temperature (Biron (2007), p.156).

Table II.3 Common Polymers' Thermal Properties

Polymer	Tg (°C)	Tm (°C)	Thermal Conductivity	HDT (°C)
Polymethyl Methacrylate (PMMA)	105	-	Low	85
Polycarbonate (PC)	147	270	Moderate	135
Polyethylene (PE)	-	130	Low	80
Polytetrafluoroethylene (PTFE)	-	327	Very Low	260
Polyamide (PA)	45-80	250	Moderate	100-250
Polyethylene Terephthalate (PET)	70	250	Low	70-80
Polyetheretherketone (PEEK)	143	343	Moderate	160

II.4.3 Mechanical Properties

Polymers have unique mechanical properties compared to metals and ceramics, largely due to their molecular structure and the type of intermolecular forces present. These properties are highly dependent on temperature, strain rate, and environmental conditions (such as humidity and chemical exposure).

Four typical behaviors can be distinguished in the case of polymers (Figure I.6).

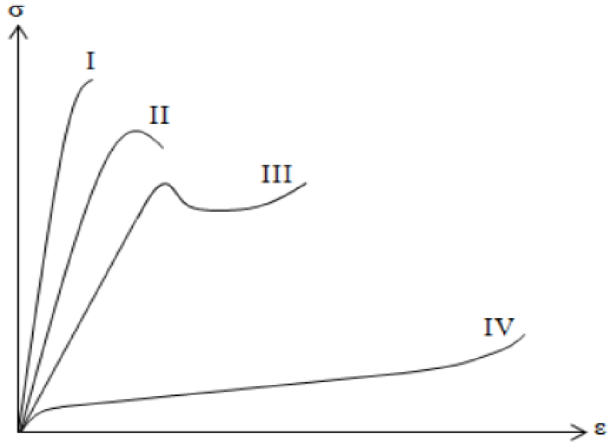


Figure. II.3: Typical Stress-Strain Curves of Polymers

Curve I displays only a linear elastic region. In this case, the material is considered brittle and fractures without undergoing any plastic deformation. If the polymer is loaded within its linear elastic range, it returns to its original shape upon unloading. Highly crosslinked thermosetting polymers typically exhibit this kind of behavior.

Most thermoplastics and thermosets tested at temperatures well below their glass transition temperature (Tg) show behavior corresponding to Curve II. These polymers have a linear elastic region followed by a limited plastic deformation zone.

When these same materials are tested at temperatures close to Tg, the plastic deformation region expands (Curve III). This is due to the stretching of the polymer chains. During stretching, the macromolecular chains align with the direction of the applied load. This reorientation reinforces the polymer, leading to a second increase in stress within the material.

Finally, Curve IV represents the behavior of elastomers, whose elasticity is nonlinear but reversible, thanks to covalent bonds between the polymer chains that allow the material to recover its original shape after deformation.

A single polymer can exhibit different behaviors depending on the temperature and the strain rate, meaning several stress-strain curves can be associated with the same material. Carswell and Nason (1944) plotted such curves for PMMA (Tg ≈ 100°C) at various temperatures (Figure I.7).

At temperatures below 40°C, PMMA behaves as a brittle or slightly plastic viscoelastic material.

When the temperature rises above 50°C, PMMA undergoes significant stretching, and its plastic deformation becomes dominant. Similarly, the lower the strain rate, the greater the plastic deformation exhibited by the polymer.

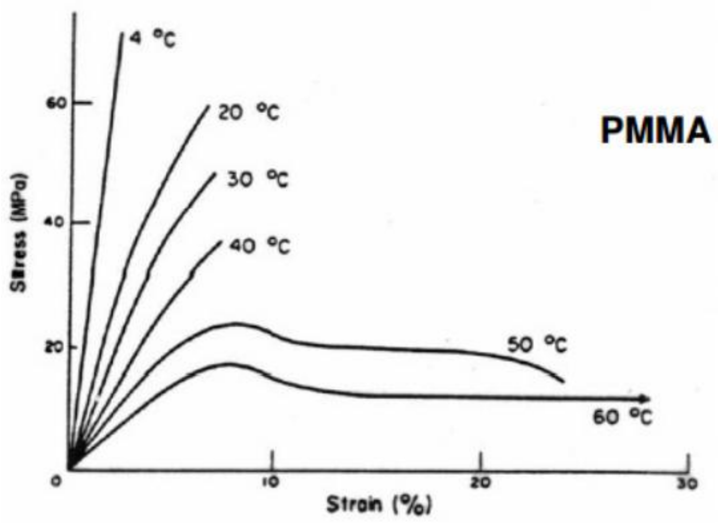
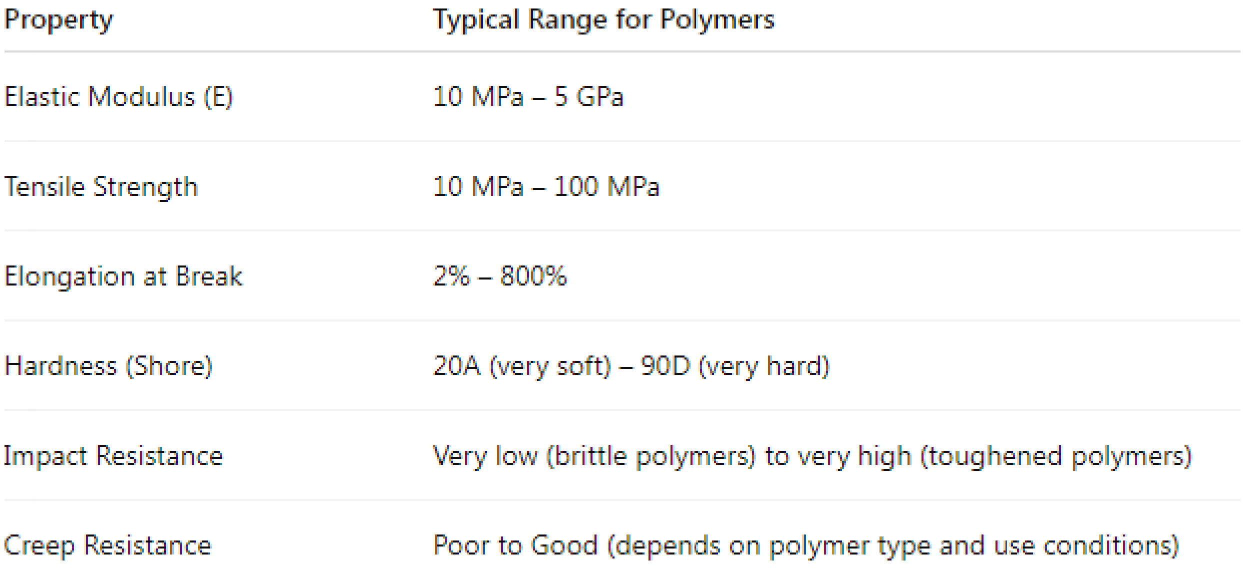


Figure. II.4: Influence of Temperature on the Stress-Strain Curve of PMMA (Carswell et Nason (1944)).

Table II.4: Typical Mechanical Property Ranges for Polymers.



Property	Typical Range for Polymers
Elastic Modulus (E)	10 MPa – 5 GPa
Tensile Strength	10 MPa – 100 MPa
Elongation at Break	2% – 800%
Hardness (Shore)	20A (very soft) – 90D (very hard)
Impact Resistance	Very low (brittle polymers) to very high (toughened polymers)
Creep Resistance	Poor to Good (depends on polymer type and use conditions)

II.5 Thermomechanical Testing

Thermomechanical analysis (TMA) is a key technique used to characterize solid and liquid materials' dimensional and mechanical behavior under controlled conditions of temperature, time, and applied force. It enables the precise measurement of properties such as the coefficient of thermal expansion (CTE), the glass transition temperature (Tg), and the compressive modulus. These measurements are essential for understanding how materials respond to thermal cycling and mechanical loading over time.

In the context of long-term behavior, materials are often subjected to accelerated aging tests to simulate extended periods of exposure to environmental factors such as heat, humidity, UV radiation, and chemical agents. These studies help predict the evolution of mechanical, thermal, and chemical properties throughout the material's service life, providing critical data for reliability and durability assessments.

Combustion behavior is another important aspect of material characterization, particularly for polymers in applications requiring high safety standards. Combustion tests evaluate flammability, smoke generation, and thermal degradation under exposure to open flame or high temperatures. Standards such as UL 94 or ISO 11925-2 are commonly used to classify materials according to their fire resistance and burning characteristics. Together, thermomechanical testing, aging analysis, and combustion studies form an integrated approach to assessing the full performance profile of materials in real-world conditions.

II.5.1 Long-Term Behavior (Aging)

The aging of polymers refers to the irreversible changes in their physical, chemical, and mechanical properties over time, influenced by a variety of environmental factors. Common causes of aging include exposure to elevated temperatures, ultraviolet (UV) and visible light, atmospheric components (such as oxygen and ozone), humidity, and liquids.

Aging processes in polymers can be classified into several categories: physical aging, chemical aging, and thermal aging, among others. As most polymers are amorphous, they naturally undergo physical and structural modifications over time. Typically, the softer and more flexible a polymer is, the more susceptible it is to time-dependent changes. Other critical factors affecting aging include the polymer's chemical composition, the presence and concentration of oxidation-prone groups, and the amount of plasticizers or additives within the material.

At the molecular level, aging involves chemical transformations that degrade macromolecules or lead to cross-linking, forming branched or three-dimensional structures. Various aging mechanisms exist; for instance, oxidative degradation is driven by a chain reaction involving the formation and breakdown of hydroperoxides. The rate of aging depends on both the polymer's intrinsic sensitivity and the intensity of external factors.

Polymers with carbon-based backbones and unsaturated bonds such as natural rubber and synthetic isoprene rubber are particularly vulnerable to oxidative aging. Aging manifests through a deterioration of mechanical properties, surface cracking, color changes, and in severe cases, complete material failure. Aging affects not only the shelf life of stored polymers but also the operational lifespan of polymer-based products.

In real-world conditions, multiple aging factors act simultaneously. For example, during atmospheric aging, polymers are exposed to a combination of oxygen, light, ozone, and humidity. Additionally, mechanical stresses, either generated during manufacturing or resulting from service conditions, significantly accelerate the aging process. To mitigate aging, stabilization techniques such as the incorporation of antioxidants, UV absorbers, and protective coatings are commonly employed.

II.5.2 Combustion

Polymeric materials are extensively used across a broad range of industries. However, due to their high combustible content, they are inherently prone to ignition and rapid flame propagation. Enhancing their fire resistance is crucial for many applications, achieved through the addition of flame retardants that either inhibit or delay combustion and reduce smoke generation.

Different flame retardants operate via various mechanisms. Some promote endothermic decomposition, absorbing heat and thereby slowing the combustion process. However, during decomposition, polymers may fragment into volatile compounds, including regenerated monomers, that are highly susceptible to oxidation and combustion. The combustion products vary depending on the polymer’s structure and burning conditions and may include carbon monoxide (CO), carbon dioxide (CO_2), hydrogen chloride (HCl), nitrogen dioxide (NO_2), organic acids, and ammonia (NH_3). Certain nitrogen-containing polymers can also release hydrogen cyanide (HCN), which is highly toxic. The toxicity of combustion gases can be significant and complicated by synergistic effects between multiple gases, compounded by the physiological impacts of reduced oxygen levels.

Strategies to improve the fire resistance of polymers are based on understanding: (1) the chemical and physical properties of the base polymer, (2) its degradation pathways, (3) its combustion behavior and dependence on degradation products, and (4) the chemical and physical properties of flame retardant additives and their interactions with the polymer matrix.

Assessing the flammability of polymeric systems and their behavior under real-world fire conditions is complex. Therefore, various semi-quantitative test methods have been developed to simulate and quantify flammability risks. Among these, the Limiting Oxygen Index (LOI) test is one of the most widely used, providing a measure of the minimum concentration of oxygen required to sustain combustion.

II.6 Polymer Processing Techniques

Plastics, or polymers intended for processing, are typically supplied in the form of liquids, powders, or pellets.

To transform them, the materials must be mixed, melted, and often combined with additives such as colorants or plasticizers, before being shaped into final products. Among the various available methods, eight major processing techniques are commonly used, with the selection depending on the desired object or packaging type.

II.6.1 Calendering

Calendering is a process primarily used to manufacture semi-finished products such as plastic films and sheets. In this technique, thermoplastic materials, often blended with additives and stabilizers, are compressed and shaped by passing them through a series of parallel rollers in a machine called a calender.

Principle

The raw material is first heated and then kneaded by a specially designed screw conveyor, transforming it into a thick, homogeneous paste. This paste is then fed into the calender, where it is progressively flattened and stretched between heated rollers to achieve the desired thickness and surface finish. The resulting sheets can be further processed or used directly in a variety of applications, such as packaging, flooring, or automotive interiors.

For gelling to occur and for the material to attain the desired mechanical properties, it is subsequently passed between two heated calender rolls. These rolls are carefully controlled based on several critical parameters, including:

- ✓ Roller temperature
- ✓ Applied pressure
- ✓ Rotation speed

By adjusting these settings, operators can finely control the thickness, surface texture, and uniformity of the final sheet. The spacing between the rolls, the pressure exerted, and the type of roller surface all influence the dimensions and surface finish (e.g., smooth or textured grain) of the films produced. Once formed, the continuous plastic film can either be wound into rolls for storage and transport or cut into sheets of specified dimensions and thickness, ready for downstream processing.

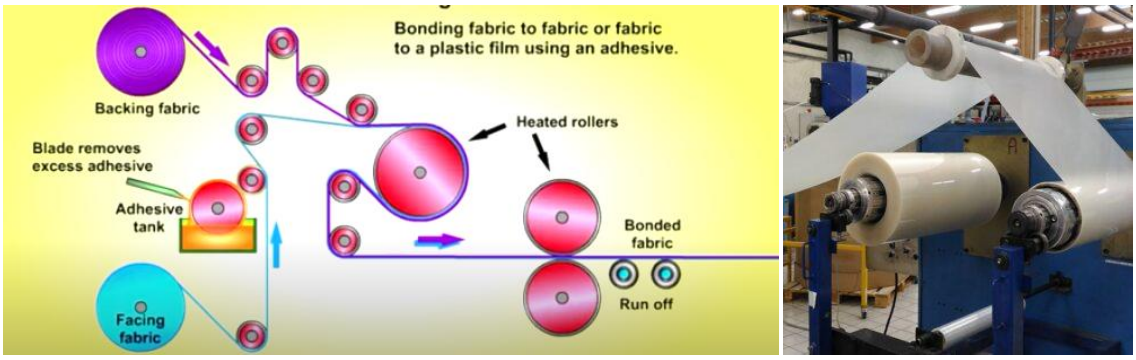


Figure. II.5: Polymer processing techniques with calendering.

Applications

Calendering is widely used to produce semi-finished plastic products, including:

- ✓ Sheets and films: These can be further transformed into final products such as containers, trays, or cups through secondary processing techniques like thermoforming.
- ✓ Decorative and technical laminates: For furniture, flooring, and automotive interiors.
- ✓ Coated fabrics and membranes: For industrial or consumer applications where flexible and durable materials are required.

II.7.3 Thermoforming

Behind this technical term lies a versatile manufacturing process used to produce a wide variety of hollow or shaped objects. In the packaging industry, thermoforming is commonly used to create trays, cups, yogurt containers, and many other products.

Principle

Thermoforming is a molding technique in which a plastic sheet is heated until it becomes soft and pliable, then shaped over or into a mold by applying pressure, vacuum, or mechanical force. Once the material conforms to the desired shape, it is cooled to retain the form and solidify the final product.

The typical steps involved in thermoforming are as follows:

Heating: A plastic sheet (previously extruded or calendered) is uniformly heated, typically using infrared heaters, until it reaches its forming temperature just above its glass transition or melting point depending on the polymer type.

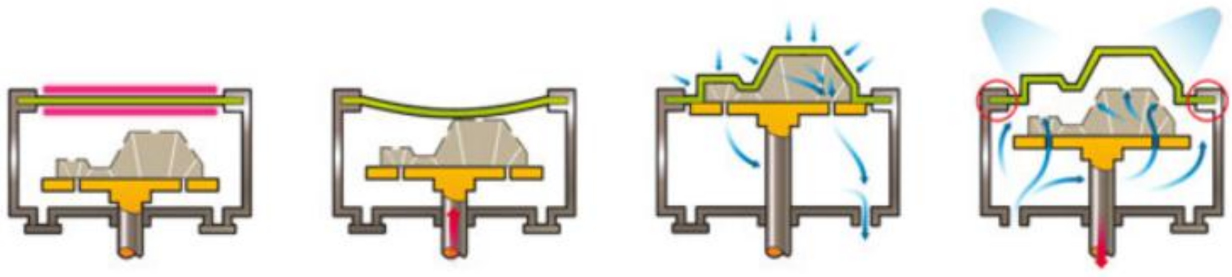


Figure II.6: Polymer Processing Techniques: Typical Steps in Thermoforming.

1. Forming: The softened sheet is then immediately positioned over a mold.
2. Forming can be achieved by: Vacuum forming: where air is evacuated between the sheet and the mold, pulling the plastic tightly against the mold surface.
3. Pressure forming: where additional positive air pressure is applied to push the sheet onto the mold.
4. Mechanical forming: where mechanical tools assist in stretching the sheet over complex mold geometries.
5. Cooling and Setting: After forming, the material is cooled either naturally or using cooling systems to solidify and stabilize the shape.
6. Trimming: Excess material around the formed part is cut away, and the finished product is collected for further use or packaging.

Applications

Thermoforming is widely used across numerous industries due to its flexibility, efficiency, and ability to create lightweight, durable products. Common applications include:

- ✓ **Toys**: Large molded items such as sandpits, playground slides, and toy storage bins are often produced by thermoforming, offering robust yet lightweight structures suitable for children.
- ✓ **Food Packaging**: Products like yogurt pots, disposable cups, and food trays (barquettes) are typically manufactured through thermoforming, providing hygienic, protective, and cost-effective packaging solutions.
- ✓ **Blister Packaging**: Used extensively in the pharmaceutical, electronics, and retail sectors, thermoformed blister packs securely enclose products while offering clear visibility for consumers.
- ✓ **Disposable Tableware**: Items such as plastic cups, plates, and catering trays are thermoformed to combine low production costs with easy handling and transport.

II.7.4 Injection Molding

Many of the plastic toys and figurines you know such as Playmobil® and LEGO® are created using a manufacturing technique known as injection molding. Injection molding is a highly versatile process that enables the mass production of molded objects with complex shapes and precise details. It is particularly well-suited for producing parts in both very small and very large sizes, ranging from just a few tenths of a gram to several kilograms.

Principle

Before becoming the intricate toys we recognize, items like Playmobil® figures and LEGO® bricks started as simple plastic pellets.

The injection molding process involves several key steps:

1. Melting: The raw plastic material, usually in the form of small granules or pellets, is fed into a heated barrel where it is melted into a viscous fluid by the combined action of heat and a rotating screw.
2. Injection: Once the material reaches the correct viscosity, it is rapidly injected under high pressure into a steel mold cavity. The mold precisely defines the final shape of the product, even capturing fine surface textures or complex geometries.
3. Cooling: Inside the mold, the molten plastic cools and solidifies into the shape of the cavity. Cooling channels within the mold help speed up this process by circulating a cooling fluid.
4. Ejection: After sufficient cooling, the mold opens, and ejector pins push the finished part out of the mold. The cycle then repeats, enabling very high production rates.

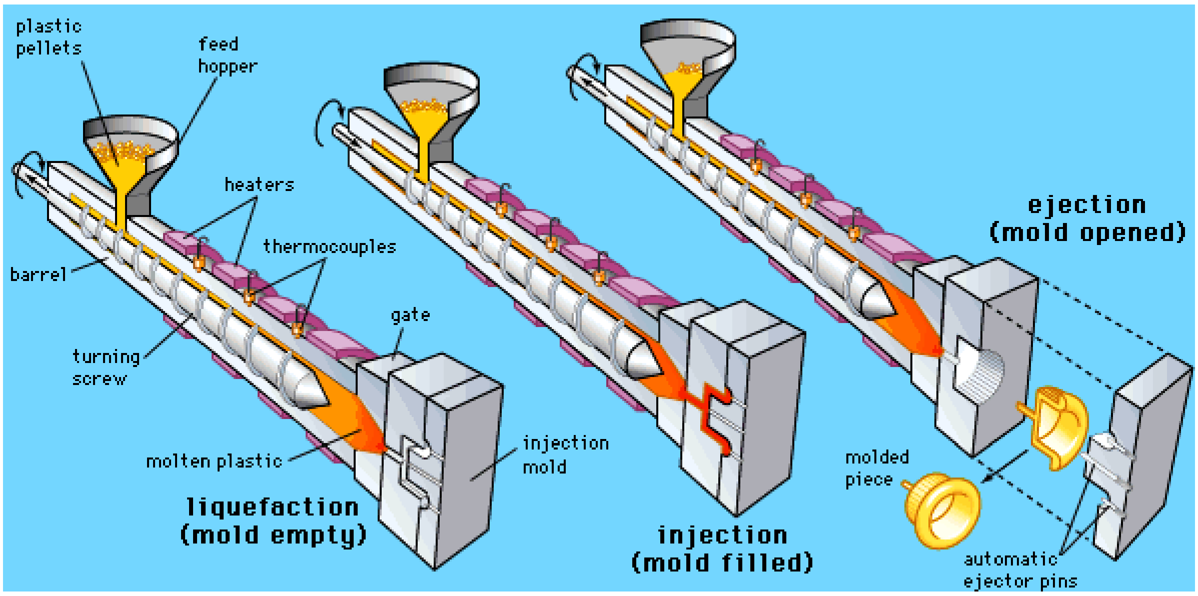


Figure II.7: Polymer Processing Techniques: Typical Steps in the Injection Molding of Thermoplastic Polymers.

Applications

Injection molding is one of the most widely used plastic processing techniques due to its precision, speed, and scalability. It enables the production of complex parts with high dimensional accuracy and excellent surface finish. The versatility of the process allows it to be applied across a wide range of industries, including:

- Toys and Consumer Goods

Popular products such as LEGO® bricks, action figures, and household items (e.g., containers, kitchen tools, clips) are mass-produced using injection molding, taking advantage of its ability to replicate fine details and produce durable parts efficiently.

- Automotive Industry

Injection-molded components are used extensively in vehicle interiors and exteriors, including dashboards, grilles, handles, light housings, and functional under-the-hood components, due to their strength, precision, and cost-effectiveness.

- Medical and Healthcare

The process is used to manufacture sterile and precise medical devices such as syringes, inhalers, diagnostic components, and surgical instruments. Medical-grade thermoplastics ensure safety and biocompatibility.

- Electronics and Electrical Devices

Casings for smartphones, remote controls, plugs, connectors, and switch housings are produced by injection molding, offering electrical insulation, flame retardancy, and design flexibility.

- Packaging

Rigid packaging components such as caps, lids, dispensers, and containers for food, cosmetics, and industrial use are often injection-molded for consistent quality and durability.

- Technical and Industrial Parts

Complex functional parts in machinery, tools, and appliances including gears, bushings, and enclosures are also manufactured by injection molding to meet mechanical and thermal performance requirements.

II.7.5 Injection Blow Molding

Injection blow molding is a plastic forming process used primarily for the production of hollow objects, such as bottles and containers, in high volumes with excellent dimensional precision and surface finish. It is especially suitable for small to medium-sized items requiring narrow necks and uniform wall thickness.

Principle

Injection blow molding combines elements of both injection molding and blow molding. The process takes place in three main stages:

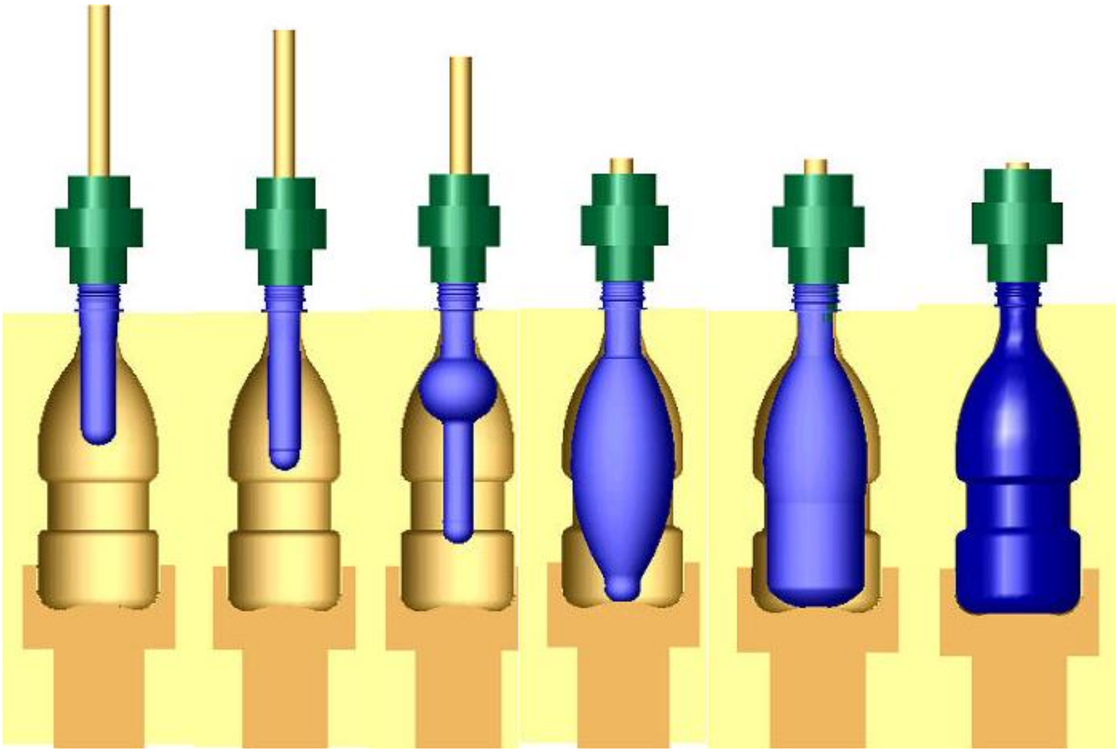


Figure II.8: Polymer Processing Techniques: Typical Steps in the Preform stretching and blowing phase

1. **Injection:**

A thermoplastic material is first melted and injected into a mold to form a preform, also known as a parison. This preform typically resembles a test tube with a finished neck and thread.

2. **Blow Molding:**

The preform is transferred to a blow mold while still warm or after being reheated. Compressed air is introduced into the interior of the preform, forcing the plastic to expand and conform to the shape of the blow mold cavity.

3. **Cooling and Ejection:**

The formed part is cooled inside the mold until it retains its final shape. It is then ejected from the mold, ready for use or further processing.

Injection blow molding is highly efficient and produces parts with precise neck dimensions and minimal flash, eliminating the need for secondary trimming.

Applications

Injection blow molding is widely used in industries where high-quality, uniform, and lightweight hollow plastic products are needed. Common applications include:

1. **Packaging**:

- Bottles for pharmaceuticals (e.g., pill bottles, syrups)
- Personal care products (e.g., shampoo, lotion bottles)
- Small beverage bottles and food containers

2. **Medical and Laboratory Equipment:**

- Vials, droppers, and sample containers.
- Single-use laboratory bottles.

3. **Cosmetics:**

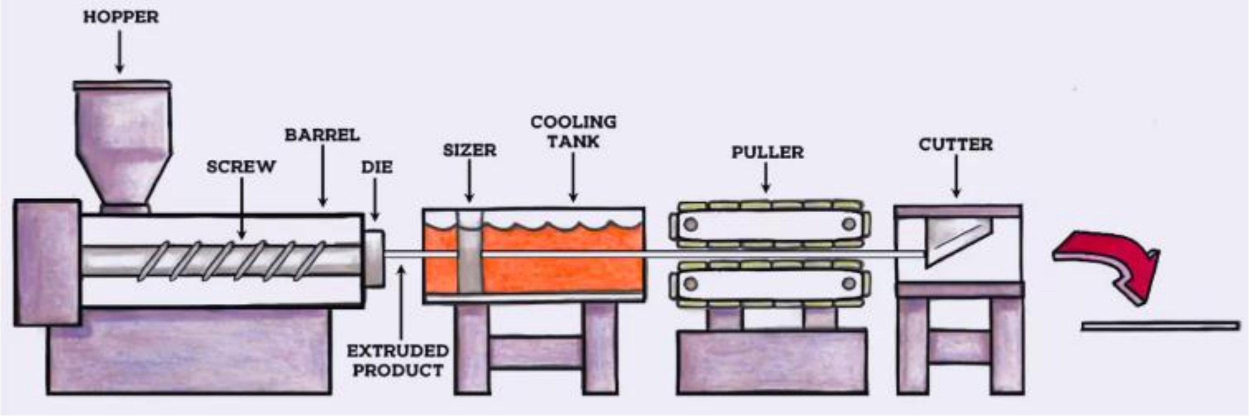
- Containers for creams, perfumes, and essential oils.
- Compact and travel-sized packaging

II.7.6 Extrusion

Extrusion is a continuous manufacturing process widely used in the plastics industry to produce objects with a constant cross-sectional profile. It is particularly suited for forming long parts such as tubes, pipes, films, profiles, and sheets. The process is efficient, scalable, and highly adaptable to various thermoplastics.

Principle

The extrusion process involves the following key steps:



(a)

(b)

Figure II.9: (a): Plastic extrusion continuous process explained, (b) : Extruder for the production of polyethylene pipes.

1. **Feeding:**

Thermoplastic materials, usually in the form of pellets or granules, are fed into the hopper of the extruder.

2. **Melting and Homogenizing:**

The material is conveyed through a heated barrel by a rotating screw. As the plastic advances, it melts due to the combination of friction, pressure, and external heating, forming a homogeneous molten mass.

3. **Shaping:**

The molten polymer is forced through a specially designed die at the end of the barrel. The shape of the die determines the cross-section of the extruded product.

4. **Cooling and Solidifying:**

Once the material exits the die, it is cooled — typically using air or water baths — to solidify and retain the desired shape.

5. **Cutting or Rolling:**

The continuous profile is then either cut into specified lengths (for pipes or profiles) or wound into rolls (for films or sheets). Extrusion is a continuous process, allowing for high output rates and minimal material waste.

Applications

Extrusion is used in a wide range of industrial sectors due to its versatility and efficiency. Common applications include:

1. **Construction and Infrastructure:**
- PVC pipes for plumbing and drainage.
- Window frames, weatherstripping, and siding.
- Electrical conduit and cable insulation

2. **Packaging:**
- Plastic films for food wrapping.
- Blister packaging and shrink films.
- Laminated sheets and multi-layer barrier films

3. **Consumer Goods:**
- Garden hoses, tubes, and flexible profiles.
- Curtain rails, sealing strips, and decorative trims

4. **Automotive:**
- Door seals, trim strips, and underbody panels.
- Wire and cable protection conduits

5. **Electrical and Electronics:**
- Insulated wires and cables.
- Protective sheathing for fiber optics

II.7.7 Extrusion Blow Molding (Blow Extrusion)

Extrusion blow molding is a widely used process in the plastics industry for manufacturing hollow objects. It combines the principles of extrusion and blow molding to produce items such as bottles, containers, tanks, and other hollow bodies with uniform wall thickness.

Principle

The process involves several key steps:

a) Extrusion of a Parison

Thermoplastic material (such as PE, PP, or PETG) is melted in an extruder and extruded vertically in the form of a hot, hollow tube known as a parison.

b) Mold Closing

A two-part mold closes around the parison, clamping it at both ends to seal it.

c) Blow Molding

Compressed air is introduced inside the parison, inflating it so that it conforms to the inner shape of the mold cavity.

d) Cooling and Ejection

The shaped part is cooled within the mold. Once solidified, the mold opens and the finished product is ejected.

e) Post-processing (if necessary)

Operations such as trimming, deflashing, or drilling may be performed to finalize the product.

Applications

Extrusion blow molding is ideal for the mass production of hollow plastic parts. Common applications include:

Packaging

- Bottles for beverages (milk, juice, water)**.**
- Containers for household and cosmetic products (detergents, shampoos, lotions)**.**
- Jerrycans and chemical drums

Automotive Industry

- Fuel tanks.
- Washer fluid reservoirs.
- Air ducts and lightweight technical parts

Toys and Leisure Items

- Hollow toys.
- Cones, balls, and floatation devices

Medical Equipment

- Disposable plastic containers and sterile bottles

II.8. Polymerization by addition or condensation

II.8.1 Chain Polymerization (Addition Polymerization)

Definition:

Chain polymerization involves the growth of polymer chains through the successive addition of monomer molecules containing double bonds (usually vinyl-type monomers). It proceeds via a chain reaction mechanism that includes initiation, propagation, and termination steps.

Mechanism:

- Initiation: A reactive species (radical, cation, or anion) is generated, typically by heat, light, or a chemical initiator.
- Propagation: The active center adds monomers one by one, rapidly growing the polymer chain.
- Termination: The active chain ends are deactivated by combination or disproportionation.

Key Features:

- Fast chain growth.
- High molecular weight polymers formed early in the reaction.
- Requires unsaturated monomers (C=C double bonds).

Examples:

Polyethylene (PE): Made from ethylene ($CH_2=CH_2$).

- Initiation: A radical attacks an ethylene molecule.
- Propagation: $CH_2–CH_2\bullet$ adds more ethylene units.
- Termination: Two radicals combine.

Polystyrene (PS): Made from styrene ($CH_2=CH–Ph$).

- Poly(methyl methacrylate) (PMMA): Made from methyl methacrylate.
-

II.8.2 Step-Growth Polymerization (Polycondensation)

Definition:

In polycondensation, monomers with two or more functional groups (e.g., –COOH, –OH, $–NH_2$) react with each other, forming covalent bonds and releasing small molecules like water, methanol, or HCl as by-products.

Mechanism:

- Monomers react in a stepwise fashion.
- Any two molecules monomer, oligomer, or polymer can react at any time.
- High molecular weights are achieved only near the end of the reaction when conversion is almost complete.

Key Features:

- Slower polymer growth.
- Produces by-products.
- Requires functionalized monomers (not necessarily unsaturated).

Examples:

Polyesters: e.g., PET (polyethylene terephthalate) from terephthalic acid and ethylene glycol.

- Reaction: $HO–CH_2–CH_2–OH + HOOC–C_2H_2–COOH \rightarrow PET + H_2O$

Polyamides: e.g., Nylon-6,6 from hexamethylenediamine and adipic acid.

Polyurethanes: Formed from diisocyanates and polyols.

Chapter III Glass and Ceramics

III.1 Introduction

Glass and ceramics are essential materials in both traditional and advanced technological applications due to their unique combinations of mechanical, thermal, electrical, and optical properties. While both belong to the category of inorganic, non-metallic solids, they differ significantly in structure and behavior. Glasses are amorphous materials, lacking long-range atomic order, whereas ceramics typically exhibit a crystalline microstructure. These materials are widely used—from architectural and domestic products to critical components in aerospace, electronics, and biomedical engineering. This chapter explores the fundamental structures, manufacturing processes, property profiles, and degradation mechanisms of glass and ceramics, offering a comprehensive understanding of their behavior and applications in modern industry.

Modern research into the physics and chemistry of ionic glasses began alongside the earliest systematic efforts to formulate new glass compositions (see Fig. 1). Initially, these two scientific trajectories developed in relative isolation. Glass formulation advanced rapidly due to industrial needs, driven by pioneers such as Otto Schott, who introduced rigorous methodologies that laid the foundation for modern glass engineering and manufacturing by O. Schott et al (1875). In contrast, investigations into the fundamental behavior of glasses were led by crystallographers and geophysicists, motivated by basic scientific questions. Notably, Victor M. Goldschmidt and his student W. H. Zachariasen made seminal contributions to crystal chemistry, establishing principles that remain essential today for predicting glass-forming chemistries and understanding glass structure by V.M. Goldschmidt et al (1926).

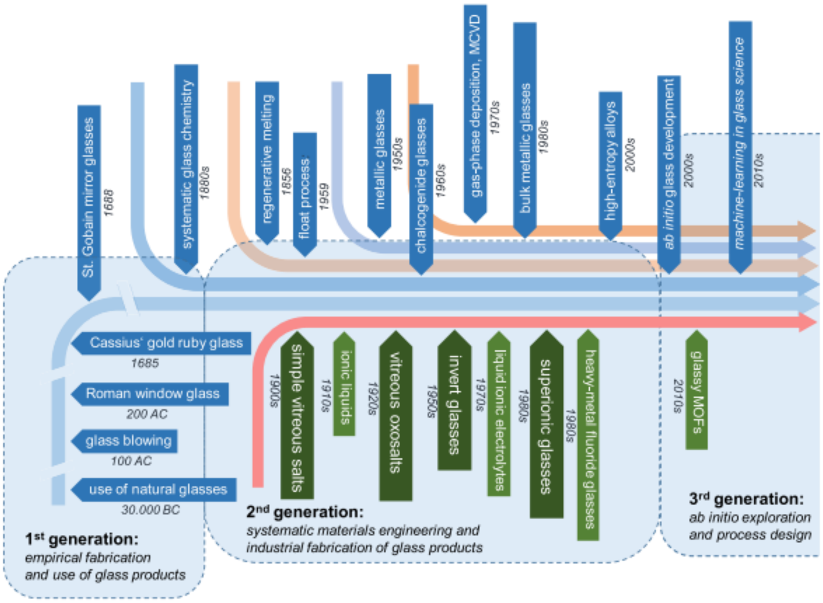


Figure III.1: Timeline of glass chemical development and glass engineering. Ionic glasses and related materials are highlighted in green O. Schott et al (1875).

III.2 Definition of a Glass – Reformulated

A glass is not defined by its chemical composition, but rather by its structural and physical behavior. While traditional glasses used throughout history were primarily silica-based, silica is not essential to glass formation. In fact, many inorganic glasses exist that contain no silica at all. Additionally, the formation of glass is not limited to cooling from a molten state; glasses can also be produced through vapor deposition, sol-gel processes, or even neutron irradiation of crystals. Although most conventional glasses are inorganic and non-metallic, there are now many organic and increasingly metallic glasses in use.

III.3 Structural Theories of Glass Formation

One of the earliest and simplest theories explaining glass formation was proposed by Goldschmidt, who observed that compounds with the general formula R_2O tend to form glass more readily when the ionic radius ratio of the cation (R) to the oxygen anion lies between 0.2 and 0.4. This ratio typically results in a tetrahedral coordination, where each cation is surrounded by four oxygen atoms. From these empirical observations, Goldschmidt concluded that glass-forming melts must involve tetrahedrally coordinated cations, although he did not provide a theoretical basis for why this structural arrangement promotes glass formation.

Mineral glasses are non-crystalline, amorphous solids, usually produced by rapidly cooling molten materials to prevent the atoms from organizing into a regular crystal lattice. While silica (SiO_2) is the primary component in most glasses, additional oxides such as sodium oxide (Na_2O), calcium oxide (CaO), and boron oxide (B_2O_3) are commonly introduced to adjust the physical and chemical properties of the glass. The disordered atomic arrangement results in key characteristics such as optical transparency and isotropic behavior (uniform properties in all directions). Structurally, the elements within glass are typically categorized as network formers (which build the glass framework), modifiers (which alter the structure and lower the melting point), and intermediates (which can act as either, depending on composition).

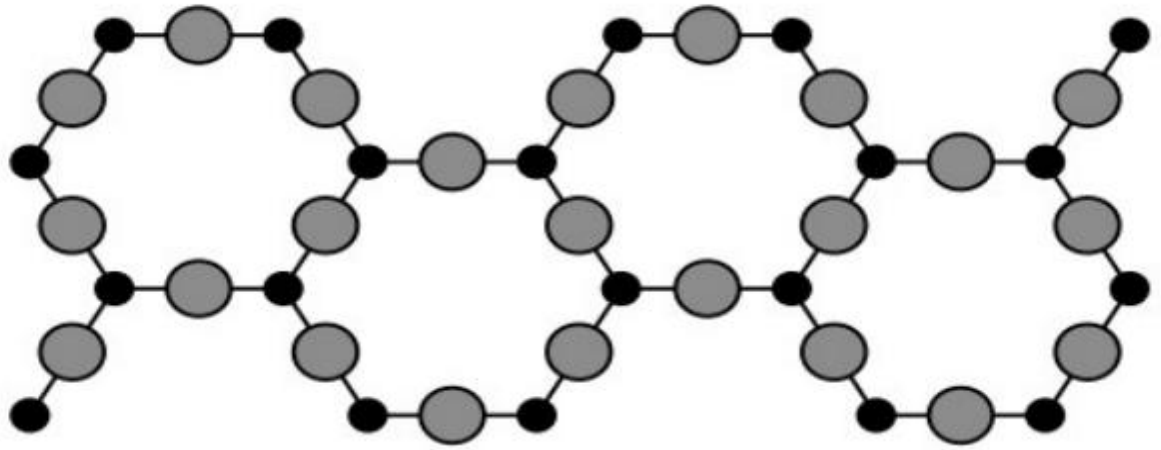


Figure III.2 : Crystalline silica (cristobalite). Zarzycki.J et al (1982).

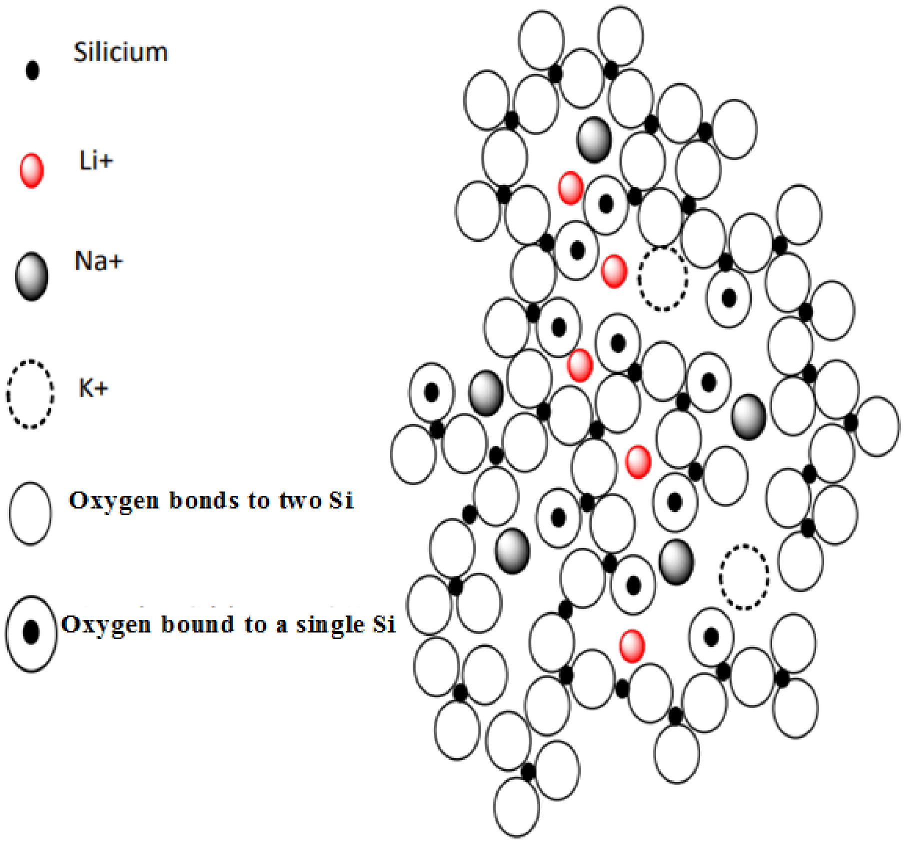


Figure III. 3 : Vitreous silica Zarzycki.J et al (1982).

III.4. Fabrication and forming of glass

The process of manufacturing and shaping glass involves several essential stages, beginning with the preparation of raw materials and ending with the formation of the final product. The objective is to create glass with tailored mechanical, thermal, and optical properties that suit its intended use.

In contrast to ceramics, glass becomes increasingly ductile when heated, undergoing a glass transition a gradual change from a rigid solid to a softened, workable state. As a result, full melting is not always required for shaping, depending on the method used. While pure silica melts at approximately 1800°C, this temperature can be significantly reduced by incorporating fluxing agents, allowing the glass to be blown into molds, pressed, or cast.

Glass products are typically classified into three main categories:

- Flat glass, used for items like windows and mirrors,
- Hollow glass, such as bottles, cups, and light bulbs,
- Glass fibers, employed in insulation and composite materials.

III.4.1 Flat Glass Manufacturing

(a) Rolling Process

In the rolling process, molten glass exiting the furnace flows over a weir and is directed between water-cooled metal rollers that solidify it into a continuous ribbon, typically 3 to 15 mm thick and up to 3.6 meters wide. This ribbon is then guided through an annealing lehr, where internal stresses are gradually relieved. The resulting raw glass sheet is not yet optically clear nor perfectly flat. Therefore, it undergoes subsequent grinding and polishing operations, which refine its surfaces to be optically transparent, flat, and parallel. The final product, known as plate glass, is characterized by its smooth finish and high visual clarity, making it suitable for demanding architectural and optical applications.

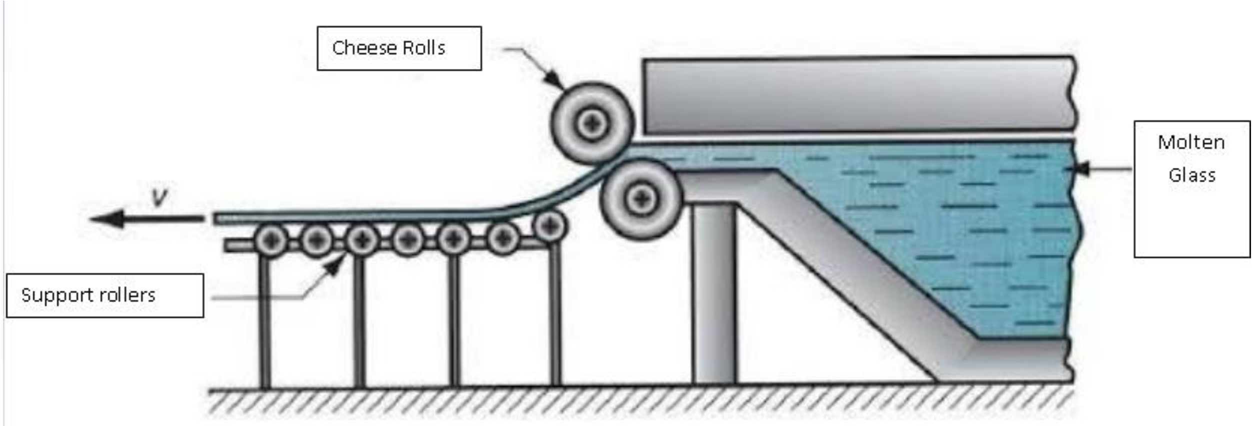


Figure III. 4 : Continuous casting.

(b) Drawing Process

In the drawing process, a solid rod or plate is vertically immersed into molten glass and then slowly withdrawn. As it is lifted, a portion of the molten glass adheres and rises with it, gradually cooling and thickening until a rupture occurs in the emerging section. The progressive increase in viscosity within the drawn "bulb" region supports the upward extension of the glass.

However, surface tension acts to narrow the sheet and eventually causes it to break. To enable continuous and stable sheet drawing, the edges of the nascent glass sheet are selectively cooled, creating a rigid frame that stabilizes the width and prevents premature rupture. This controlled solidification at the boundaries is essential for maintaining dimensional consistency and uninterrupted production in vertical glass drawing systems.

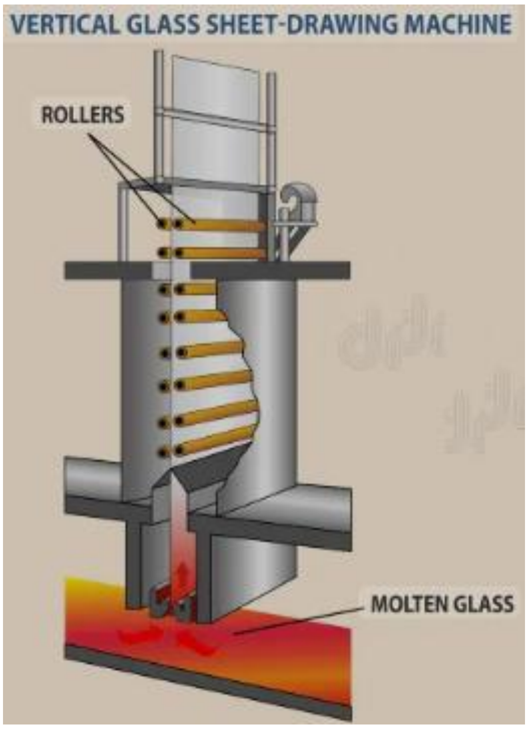


Figure III. 5 : Continuous casting.

This drawing technique is used for the continuous production of flat glass sheets with acceptable flatness for common applications, such as window glass. To enhance quality, consistency, and process control, several technical variations have been developed. These include improvements to the cooling system, adjustments to the drawing speed, and lateral guidance of the glass sheet all aimed at optimizing the width and thickness while minimizing surface defects.

Several key technological developments have shaped the continuous production of flat glass. One of the earliest was **the Fourcault process (1904),** in which a refractory block equipped with a longitudinal slit called a "debiteuse" is partially immersed in the molten glass bath. As the glass flows through the slit, it forms a bulb. A metal rod initiates the drawing process, pulling the forming sheet vertically. Asbestos rollers support the glass while non-contact radiative coolers freeze the sheet's edges to stabilize its width. The glass then passes through a vertical annealing pit before being cut to size (Fig. III.6-1).

In the Pittsburg process (1925), the debiteuse is replaced with a fully submerged refractory block that locally cools the glass. This innovation removes the mechanical constraint of the slit, allowing for higher drawing speeds and reducing surface defects associated with the Foucault method. (Fig. III.6-2)

The Libbey–Owens process (1917) also eliminates the debates. In this method, the drawn glass sheet is bent at a right angle roughly one meter above the glass bath, using a polished chromium-nickel alloy roller. This redirection reduces the vertical footprint of the facility compared to earlier methods (Fig. III.6-3)

A major leap in glass production came with **the float process (1959),** developed by the Pilkington company. In this technique, a continuous ribbon of softened glass is deposited onto a bath of molten tin. The underside of the ribbon acquires the mirror-like smoothness of the tin surface, while surface tension flattens the top surface, resulting in highly planar glass with minimal finishing requirements. This method revolutionized the flat glass industry and remains the standard today (Fig. III.7).

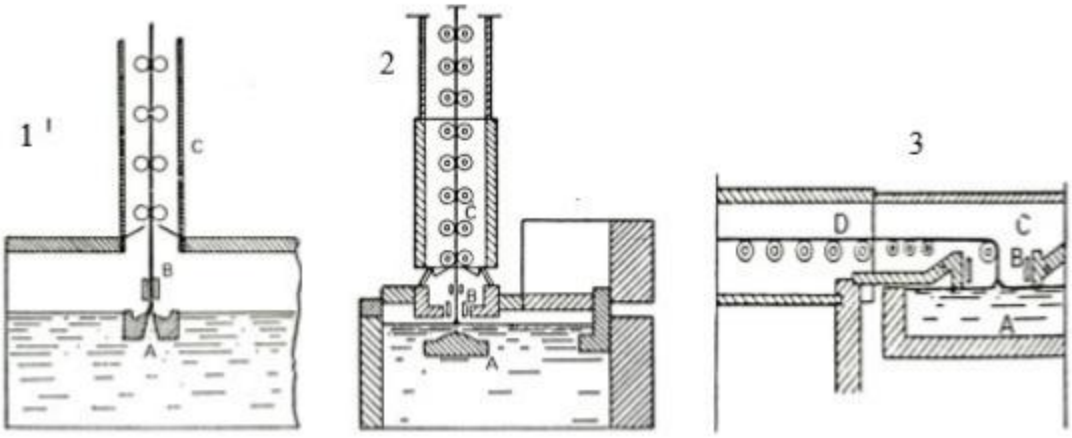


Figure III. 6 : Window glass drawing processes 1) Fourcault, 2) Pittsburgh, 3) Libbey–Owens.

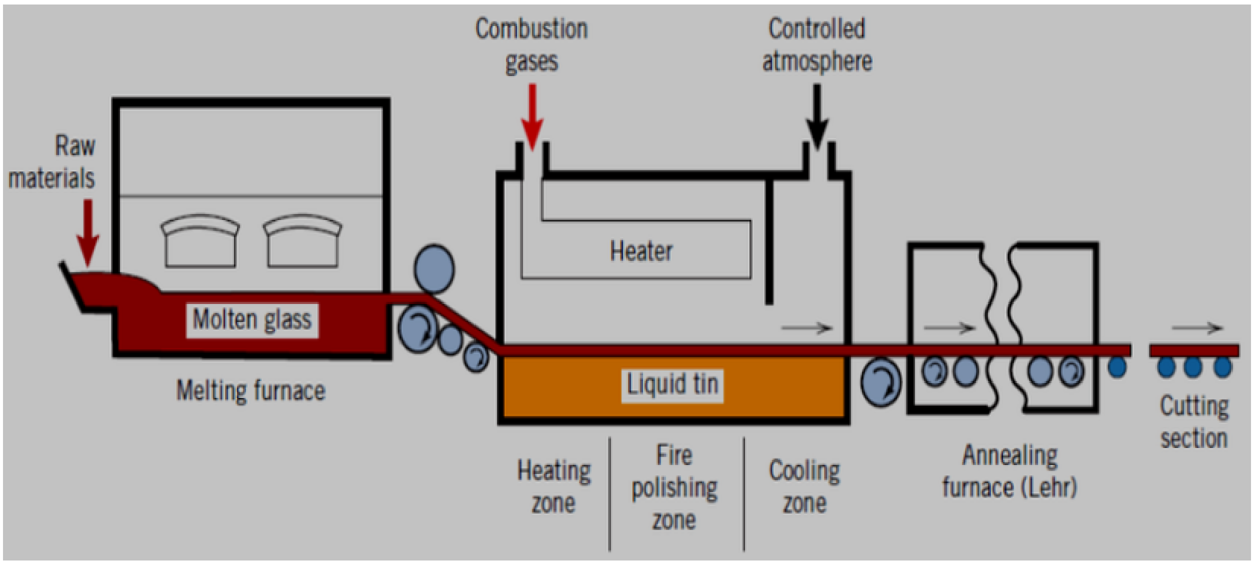


Figure III. 7 : Schematic diagram showing the float process for making sheet glass (Callister and Rethwisch, 2009)

III.4.2 Hollow Glass Manufacturing

a) Pressing Technique (Fig. III.19)

In the pressing process, a precisely measured quantity of molten glass, known as a "parison," is introduced into a mold and shaped by mechanical pressure at temperatures between 400–450°C. The molds, typically made of special steel with chrome-plated surfaces, ensure durability and smooth finishing. Automated presses, often equipped with multiple mold cavities, can produce up to 1,000 pieces per hour. This method is widely used for the production of items such as glass plates, lenses, and other symmetrical hollow glass products.

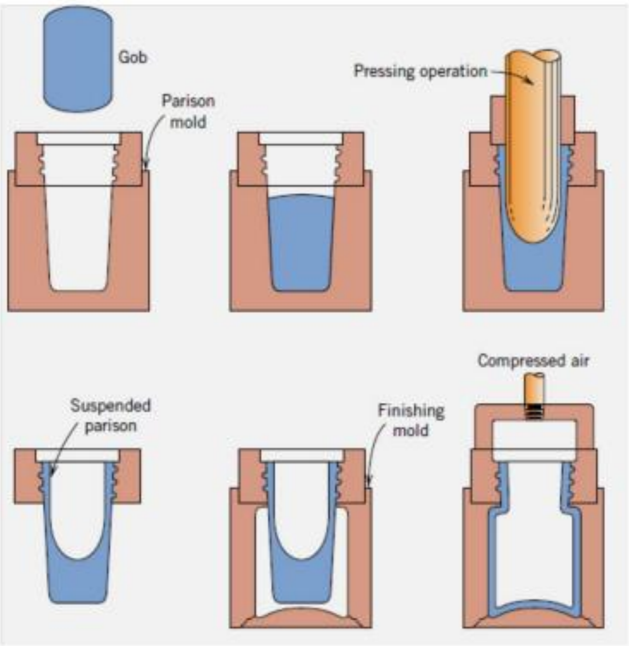
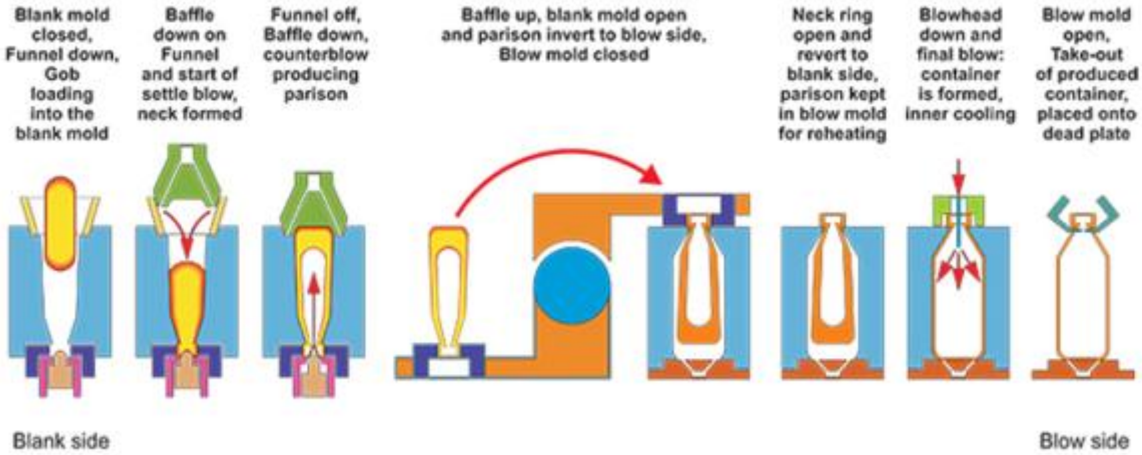


Figure III. 8 : Producing glass bottles by using the blowing method (Callister and Rethwisch, 2009).

b) Blow Molding of Hollow Glass (Fig. III.20)

Blow molding is a key technique used in the manufacture of hollow glass articles. The process typically begins with the formation of a preliminary shape known as a *parison* in a preparatory mold. This parison is then transferred into a final mold, where it undergoes the final blowing stage to achieve the desired form. Depending on how the parison is formed in the initial mold, several distinct methods are used: the **suction and blow** process developed by Owens in 1905, the **blow-and-blow** method introduced by Hartford in 1925 (Fig. III.8a), and the **press-and-blow** technique (Fig. III.8b). Each method is suited to different product requirements and offers varying degrees of efficiency and control over the final geometry and wall thickness.



(a) (b)

Figure III. 9 : Producing glass bottles by using the blowing method (Callister and Rethwisch, 2009).

III.4.2 Manufacturing of Glass Fibers

Glass can be processed into fibers for a range of applications, typically categorized into two main types: textile fibers (continuous filaments) and insulation fibers (short, entangled filaments). Three primary manufacturing principles are employed: mechanical drawing, centrifugal drawing, and fluid drawing.

a) Mechanical Drawing (Fig. III.21)

The Gossler process (1920) is a representative mechanical fiber-drawing method. It utilizes an electrically heated furnace with a perforated base containing multiple small orifices. Molten glass flows through these openings and is drawn into fine fibers by a rapidly rotating drum (Fig. III. 9). This method is especially suited for the production of continuous glass filaments used in textile and composite applications.

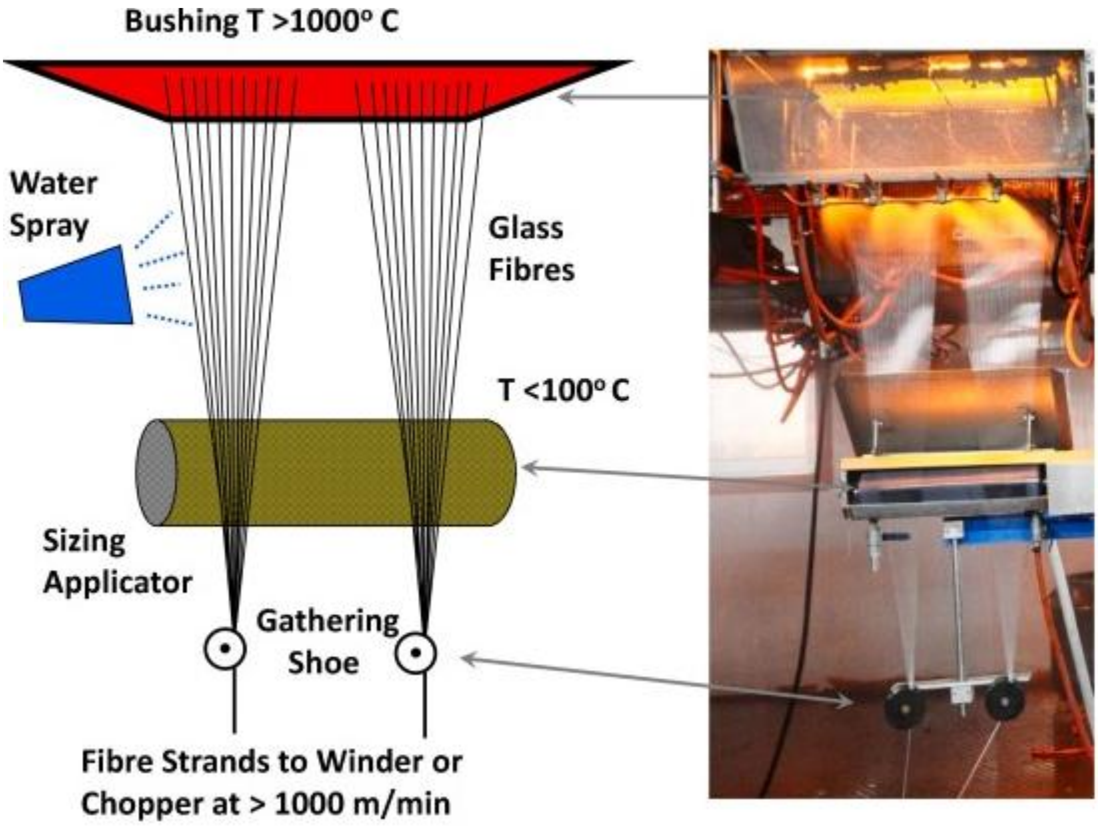


Figure III. 10 : Schematic and picture of a glass fibre forming position, Loewenstein, K. L. (1973).

b) Centrifugal Drawing

In the Hager process (1931), a stream of molten glass is directed onto a rotating refractory disc that is heated along its rim by gas flames. The centrifugal force generated by the spinning disc stretches the molten glass into fibers with diameters around 25 µm. This method is primarily used for producing short, entangled fibers suitable for thermal insulation applications.

c) Fluid Drawing (Fig. III.22)

This technique involves fragmenting thin glass filaments using high-velocity gas jets, which simultaneously stretch the glass into extremely fine fibers. Known as “superfine” fibers, these filaments typically have diameters ranging from 0.05 to 5 µm. The method is valued for producing high-quality insulating materials with superior performance characteristics.

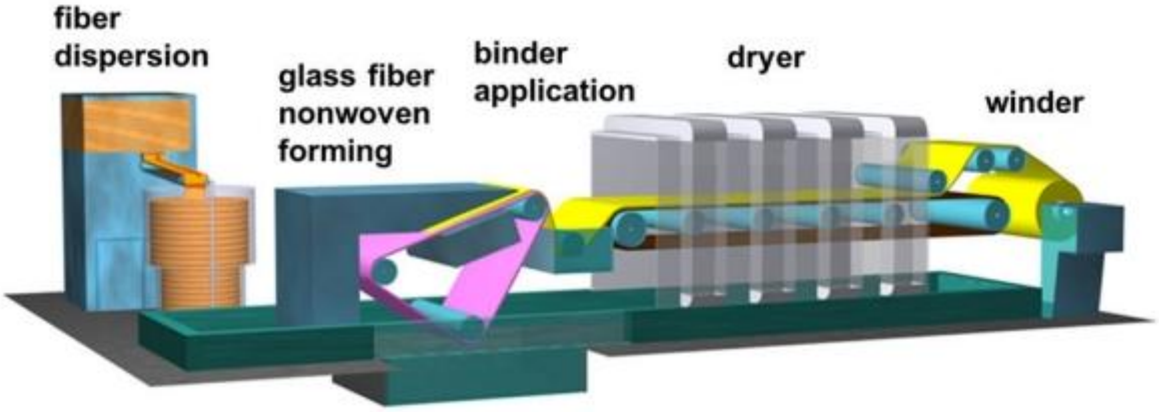


Figure III. 11 : Schematic Basic block diagram of a glass mat making process

d) Mixed Process

In certain industrial applications, a hybrid (or mixed) process combines aspects of both centrifugal and fluid drawing techniques to optimize fiber production. In this process, molten glass is first delivered onto a rotating perforated drum or disc (as in centrifugal drawing). As the glass is ejected through the perforations by centrifugal force, high-pressure gas jets or air streams are simultaneously applied to further attenuate and cool the forming filaments.

This combined approach offers several advantages:

- It enhances fiber fineness and uniformity, achieving diameters between 0.5 to 10 µm, depending on process parameters.
- The cooling and stretching via gas jets allow for better control over fiber length and diameter, improving product consistency.
- It increases production efficiency, making it suitable for both textile-grade continuous filaments and short fibers for insulation.
-

III.5. Glass Properties

Glass is a unique inorganic solid material that can be manufactured in virtually any shape or dimension while retaining its inherent transparency. Its versatility, both in structure and optical properties, makes it indispensable across a wide range of applications, from architecture to advanced optics.

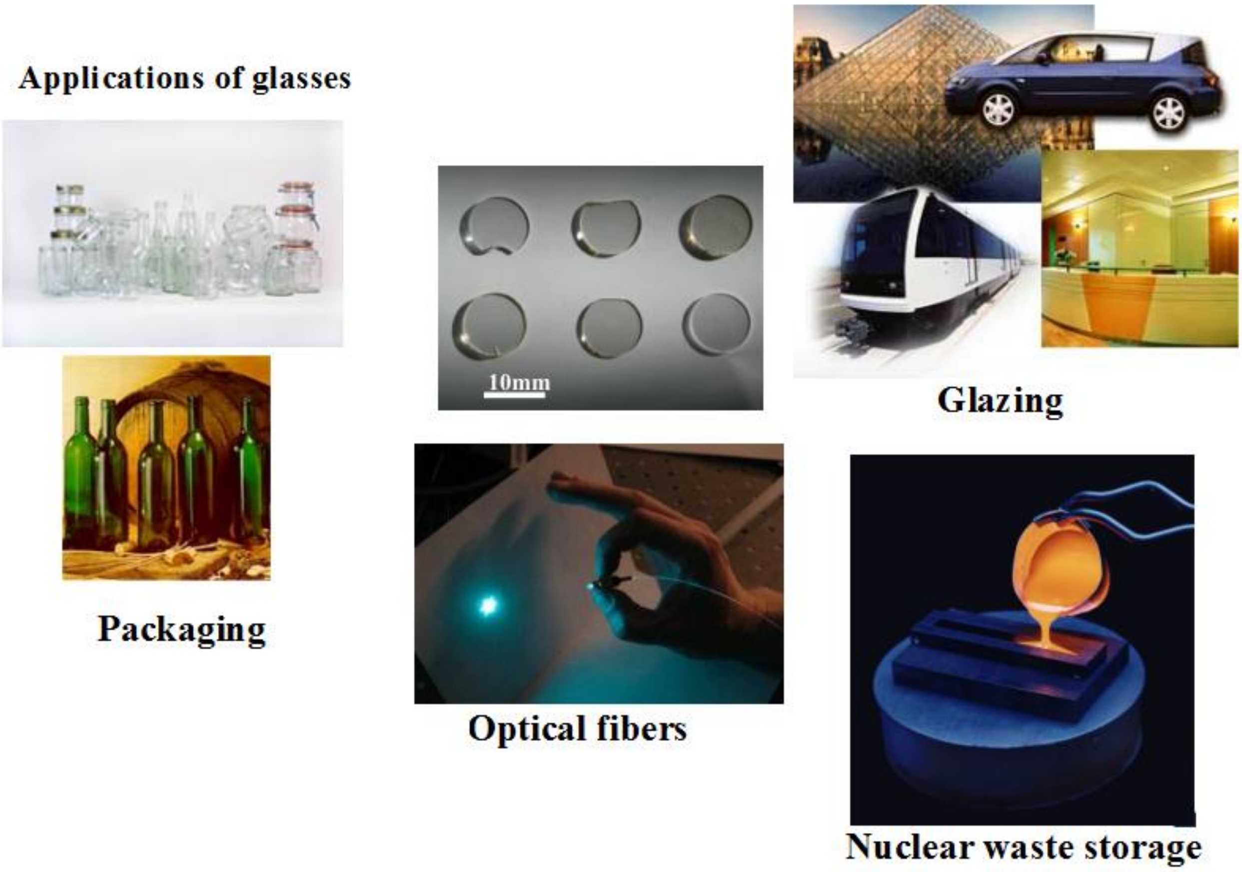


Figure III. 12 : Show the various applications of glass.

III.5.1. Physical Properties

a) **Transparency**

Glass is best known for its ability to transmit visible light, making it transparent or translucent. However, its optical appearance can be modified by chemical composition or surface treatment, resulting in materials that are opaque or opalescent. The degree of transparency is influenced by the presence of impurities and the structural uniformity of the glass matrix.

b) **Hardness**

Hardness is a measure of a material’s resistance to localized plastic deformation, typically assessed by indentation. In glass, hardness is evaluated using standard methods such as the Brinell or Vickers hardness tests, involving the penetration of a hardened steel ball or a diamond pyramid.

Two primary categories of glass can be identified based on hardness:

- **Hard glasses** possess low thermal expansion coefficients and require high temperatures to reach their softening point.
- **Soft glasses** exhibit higher thermal expansion and soften at relatively lower temperatures.

c) **Density**

The density of glass varies according to its chemical composition, with a typical value of approximately 2.5 g/cm^3. This implies:

- A cubic meter of glass weighs roughly 2.5 metric tons.
- A flat glass sheet with 1 m^2 surface area and 1 mm thickness weighs around 2.5 kg.

d) **Elastic and Mechanical Resistance**

Although brittle under tensile and flexural stress, glass exhibits significant resistance to compressive loads. The material tends to fracture under bending forces, whereas metals deform plastically. Remarkably, the compressive strength of glass is substantial — it can withstand pressures of up to 100 MPa (approximately 10 tons per cm^2) before rupture. The maximum crack propagation speed (Vm) in glass, an important factor in dynamic fracture mechanics, can be expressed by specific fracture mechanics equations depending on the stress intensity and material toughness, as discussed in J. Phalippou (2006)

III.5.2. Thermal Properties

a) Thermal Expansion:

The linear thermal expansion of glass is characterized by a coefficient of approximately 9×10^{-6} K^{-1}. This means that a glass pane measuring 2 meters in length will expand by approximately 0.54 mm when subjected to a 30°C temperature increase. Thermal shocks abrupt temperature variations can induce severe internal stress due to the non-uniform heating of the material, potentially causing fracture. This fragility under rapid thermal fluctuation limits its use in environments with abrupt temperature changes by Glas Trosch Holding AG et al. (2013).

b) Specific Heat Capacity:

The specific heat capacity of glass represents the amount of energy required to raise the temperature of one kilogram of material by one kelvin. For typical soda-lime glass, the value is approximately 800 J/kg·K. This moderate heat capacity allows glass to heat and cool gradually, which is advantageous in many thermal applications.

c) Comparative Expansion Example:

A 1-meter-long glass sheet subjected to a 100°C temperature increase would elongate by 0.9 mm, compared to 2.4 mm for aluminum under the same conditions illustrating the relatively low thermal expansion of glass by H. Scholze (1974)..

d) Thermal Conductivity:

Glass is a poor thermal conductor, with thermal conductivity values typically around 1 W/m·K, approximately 500 times lower than copper. This low conductivity renders it an excellent thermal and electrical insulator at room temperature. However, at elevated temperatures (above 250°C), its electrical conductivity increases significantly, limiting its use as an insulator under high-temperature conditions.

III.5.3. Chemical Properties

Glass is widely recognized for its exceptional chemical inertness. It remains unreactive to most substances, which makes it an ideal material for containers and laboratory equipment.

It is resistant to most acids and bases, except for hydrofluoric acid (HF), which can etch and dissolve the silica structure of glass, and certain strong alkaline solutions, which may leach alkali ions and alter its surface.

Concrete runoff water, often alkaline, can chemically degrade glass surfaces over time, making protective coatings or design considerations necessary in architectural applications.

e) Fire Resistance and Stability:

Glass does not burn, oxidize, or chemically decompose under typical thermal conditions. It is considered non-combustible and maintains chemical stability even under prolonged exposure to high temperatures, although its mechanical properties may change due to softening.

III.5.4 Optical Properties

Glass is unique among inorganic solids in its ability to maintain transparency over a wide range of thicknesses and shapes, making it indispensable for applications in optics, architecture, and photonics. Its optical properties arise from its amorphous atomic structure, which lacks the grain boundaries and crystalline domains that typically scatter light in other materials.

a) Transparency and Light Transmission

Glass exhibits high transmittance in the visible spectrum (typically 80–90% for clear soda-lime glass), owing to its low absorption and scattering coefficients. The absence of free electrons and the large bandgap (typically 8–9 eV) prevent electronic transitions in the visible range, allowing visible light to pass through with minimal attenuation.

However, the transparency of glass can be influenced by:

- **Composition**: The presence of iron, for instance, can introduce a green tint and reduce transparency in the blue and UV regions.
- **Thickness**: Light attenuation increases with thickness due to internal reflections and minor absorption.
- **Surface Quality**: Polished or coated surfaces reduce reflection losses and enhance clarity.

b) Refractive Index

The refractive index of glass varies with composition, typically ranging from 1.45 to 1.9. This property determines how light bends when entering the glass and is critical in lens design, fiber optics, and photonic devices. Dispersion, or the variation of refractive index with wavelength, must also be managed to minimize chromatic aberrations in precision optical systems.

c) Color and Opacity

Glass can also be engineered to be opaque, translucent, or colored by introducing metal oxides or by altering its microstructure. For instance:

Titanium dioxide (TiO_2) and zirconia (ZrO_2) can induce opalescence.

Cobalt oxide imparts a deep blue coloration.

Selenium and cadmium compounds yield reds and yellows.

These variations are widely exploited in artistic glasswork, architectural glazing, and signal indicators.

d) Ultraviolet and Infrared Behavior

Standard soda-lime glass absorbs UV light below ~300 nm, providing natural protection against harmful UV radiation. Conversely, it is generally opaque to infrared radiation, though specialty glasses (e.g., IR-grade chalcogenide glasses) are formulated for IR transparency in defense and thermal imaging applications.

III.7. Chemical Degradation of Mineral Materials

Most mineral-based materials exhibit high chemical stability due to the presence of strong ionic or covalent bonds. Nevertheless, certain chemical interactions can occur under specific environmental conditions. For example, in mineral glasses, alkali metal ions such as Na^+ or Ca^{2+} are subject to slight dissolution in water, which can alter the surface chemistry over time. In contrast, highly basic solutions containing hydroxide ions (OH^-) can hydrolyze the silica network at the glass surface, leading to surface dulling or opacity.

In cement-based materials, sulfate ions (SO_4^{2-}) present in water can chemically react with tricalcium aluminate (C_3A) in the cement matrix to form calcium sulfoaluminate and, in some cases, gypsum ($CaSO_4 \cdot 2H_2O$). These reactions are accompanied by a significant increase in volume, which induces internal stresses and leads to surface spalling and cracking in concrete structures.

III.7. 1 Chemical Degradation of Ceramics

Although ceramics are generally known for their excellent chemical stability and inertness, certain environmental conditions can lead to gradual degradation over time. This degradation depends on the chemical composition of the ceramic, the type of environment, temperature, and exposure time.

III.7. 2 Degradation in Glasses (Amorphous Ceramics)

In silicate glasses (e.g., soda-lime glass), alkaline ions such as Na^+ and K^+ are weakly bound in the structure and can be leached out by water or humid air, especially at elevated temperatures. This leads to:

- Surface hydration
- Loss of transparency
- Mechanical weakening over time
- Strongly basic solutions (high pH) containing OH^- ions can attack the silica network itself, hydrolyzing Si–O–Si bonds and forming silanol groups (Si–OH). This alters the chemical structure at the surface and may lead to cracking or roughness.

III.7. 3 Degradation of Oxide Ceramics

Alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2) are more resistant to attack but may still undergo degradation in aggressive media:

- Hot alkaline solutions can slowly degrade alumina.
- Zirconia can undergo low-temperature degradation (LTD), also known as aging, in humid environments, leading to phase transformation from tetragonal to monoclinic and associated volume expansion and microcracking.

III.7. 4 Degradation by Sulfates and Acid Rain

Ceramics used in structural applications (tiles, bricks, porcelain insulators) can be affected by sulfate-rich environments. In particular:

- Sulfates in water can react with components in ceramic glazes or binders.
- Acid rain (containing SO_2, NOx, or CO_2) reacts with carbonate-containing ceramics, leading to the formation of soluble salts and surface erosion.

III.7. 5 Thermal-chemical degradation

At high temperatures, ceramics can react with:

- Combustion gases (CO_2, SO_2, H_2O vapor)
- Molten salts

- Oxidizing or reducing atmospheres
- These reactions can result in reduction of metal oxides, grain boundary corrosion, or evaporation of volatile components.

Chapter IV Composite Materials

IV .1.Introduction

A composite material results from the combination of two or more distinct materials at a microscopic scale, significantly smaller than that of the final component. This configuration enables the composite to be considered as a homogenized material with new, enhanced properties. Such engineered materials are referred to as composites. The number of possible material combinations is virtually limitless, making a complete classification impractical.

IV.2. Composite Materials

In the most common sense, composite materials are engineered synthetic materials developed primarily for structural applications, where mechanical performance is paramount. A composite typically consists of a reinforcement phase (e.g., particles, short fibers, or long fibers) embedded in a continuous matrix. The type, arrangement, and volume fraction of both the reinforcement and matrix can be tailored to achieve application-specific mechanical properties, and even locally optimized performance based on stress distribution within the part.

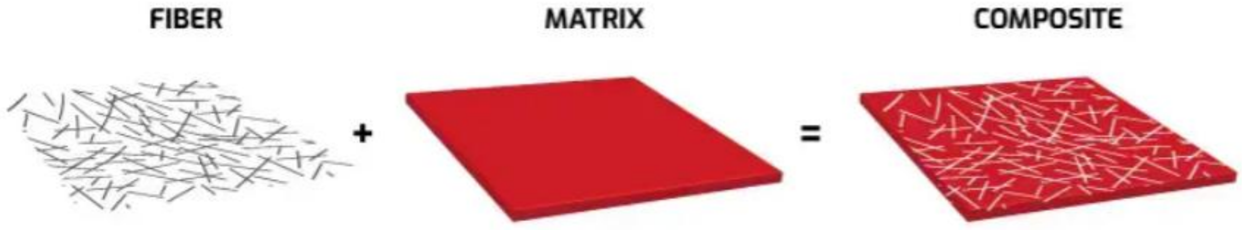


Figure IV. 1 : Principale constitution of composite.

IV.2.1. Reinforcements

The primary functions of reinforcements in a composite are to:

- Carry mechanical loads;
- Provide stiffness and tensile strength, including at elevated temperatures;
- Ensure chemical compatibility with the matrix, maintaining stable interfacial adhesion over time.

Reinforcements vary by geometry (particles, spheres, short fibers, long fibers), distribution (random, 2D mats, unidirectional layers, 2D/3D woven fabrics), and material type.

a) Glass Fibers

Glass fibers are the most widely used reinforcements due to their low cost and good overall performance. They are produced by drawing molten glass into fibers with diameters ranging from 5 to 15 µm. Their tensile and flexural strength increases as the fiber diameter decreases.

Advantages:

- Good thermal and electrical resistance
- Chemical and moisture resistance
- High compatibility with organic matrices
- Economical

Limitations:

- Moderate mechanical properties (especially stiffness)
- Poor impact resistance

b) Polymer Fibers (Aramid – e.g., Kevlar®)

Due to their low density, only a few polymers yield fibers with sufficient modulus for structural reinforcement. Aramid fibers (e.g., Kevlar®) exhibit high tensile strength, excellent fatigue and impact resistance, but show poor compression and shear performance, which limits their flexural properties. They are often combined with glass or carbon fibers.

Limitations:

- Sensitive to humidity and temperature
- Degrade under long-term environmental exposure

c) Carbon Fibers

Carbon fibers are produced by pyrolysis of polymer precursor fibers under controlled atmospheres. The resulting graphitic carbon skeleton offers high modulus, high strength, and thermal stability up to 1500°C in non-oxidizing atmospheres.

Advantages:

- High tensile strength and longitudinal stiffness
- Excellent thermal resistance
- Chemically inert and corrosion-resistant

- Very low (or zero) longitudinal thermal expansion

Limitations:

- Brittle under impact and bending
- High cost
- Electrically and thermally conductive

Carbon fibers are used in pre-impregnated unidirectional fabrics for industrial and sporting goods, and in 2D/3D woven forms for aerospace and high-performance engineering.

d) Other Reinforcements

Other advanced reinforcements include metallic fibers (e.g., boron, tungsten, steel) and ceramic-based reinforcements (e.g., Al_2O_3, B_4C, SiC, Si_3N_4, BeO, TiC). These are typically used in metal matrix composites (MMC).

Despite their high stiffness and strength, their large diameters (often >100 µm) make them susceptible to bending failure. Moreover, their high cost restricts their use to specialized high-tech applications (e.g., aerospace, defense).

IV.2.2. Matrices

The matrix phase in a composite plays several essential roles:

- Encapsulates and protects the reinforcements from environmental attack
- Maintains a uniform spatial distribution of the reinforcements
- Transfers external loads to the reinforcement phase
- Defines the final shape of the composite part

a) Organic Matrices (Polymer-Based)

Synthetic polymer matrices are the most commonly used in commercial composite materials. They are often combined with glass, aramid, or carbon fibers. Although these polymers have relatively low stiffness and tensile strength, they exhibit good processability, especially in terms of fiber impregnation and molding.

Main advantages:

- Low density
- Relatively low material cost
- Chemical resistance to a wide range of agents

- Easy and rapid processing

Main limitations:

- Poor thermal resistance
- Sensitivity to humidity

Most common types:

- **Unsaturated polyester resins**: thermosetting, used mainly in construction moldings; applied in liquid state before curing; produced via polycondensation.
- **Epoxy resins**: thermosetting, similar processing but slightly more expensive; widely used in structural applications.
- **Thermoplastic polymers**: such as polypropylene and polyamide, allow thermoforming and are recyclable. Some offer good mechanical and thermal performance.
- **Elastomers**: such as polyurethanes and silicones, are also used in specific applications.

Additionally, general-purpose thermoplastics (e.g., PE, PS, PVC) are often reinforced and stiffened with short fibers, flakes, or mineral fillers (e.g., chopped glass fibers, mica, talc, silica) for the production of mass-market items.

b) Metallic Matrices

Reinforcing a metallic matrix with fibers or particles requires impregnation with a liquid alloy, which is technically challenging. In practice, aluminum alloys are most commonly used due to their low melting point, light weight, and affordability. When combined with graphite or ceramic fibers/particles, the resulting composite benefits from:

- A balance between the toughness of the metal and the stiffness of the reinforcement
- Improved mechanical properties, especially above 200 °C.
- However, the high processing cost limits their use to aerospace and high-performance applications.

c) Mineral Matrices

Ceramic matrix composites (CMCs) are developed using matrices such as carbon, Al_2O_3, SiO_2, Cr_2O_3, MgO, or SiC. They are reinforced with fibers (metal, glass, aramid, carbon, ceramic) introduced via:

- Liquid-phase impregnation followed by high-temperature and high-pressure sintering

- Chemical vapor infiltration (CVI), where reactive gases deposit matrix material between the fibers (e.g., in carbon–carbon composites)

Main advantages:

- Low density
- High-temperature resistance (refractoriness)
- Excellent compressive strength and stiffness, even at elevated temperatures
- High chemical inertness

Main limitations:

- Brittle and sensitive to impact
- Complex and costly processing
- Carbon–carbon composites are vulnerable to oxidation above 400 °C, requiring protective coatings

IV.3. General Properties of Fiber-Reinforced Composite Materials

- ✓ **Rule of Mixtures**

The overall properties of a fiber-reinforced composite are often an average of the properties of its constituent materials, weighted by their respective volume fractions. This principle is known as the rule of mixtures, and it applies to many physical and mechanical properties of the composite.

Let:

υ_r = volume fraction of the reinforcement = $\frac{volume\ \ of\ the\ reinforcement}{volume\ \ total}$

υ_m = volume of reinforcement = 1- υ_r

The density ρ_c of the composite can be expressed as:

$$\rho_c = \rho_r \,.\, \upsilon_r + \rho_m \,.\, \upsilon_m \qquad \text{(IV.1)}$$

Where:

ρ_r : density of the reinforcement

ρ_m : density of the matrix

This rule also applies to other mechanical properties such as the longitudinal Young’s modulus in a unidirectional fiber composite.

If a composite bar with continuous fibers is subjected to an axial load Fc (parallel to the fibers), the total force is distributed between the matrix and the fibers acting in parallel, so:

$$F_c = \sigma_c \, . \, S_c = F_r + F_m = \sigma_r \, . \, S_r + \sigma_m \, . \, S_m \qquad (IV.2)$$

Assuming perfect interfacial bonding, the strain is the same in both constituents:

$$\varepsilon_c = \frac{\Delta L_c}{L_0} = \varepsilon_r = \frac{\Delta L_r}{L_0} = \varepsilon_m = \frac{\Delta L_m}{L_0} \qquad (IV.3)$$

Under elastic deformation, the composite modulus E_{cL} (in the fiber direction) can be determined by combining equations (IV.2) and (IV.3). If the cross-sectional area fractions of the fiber and matrix correspond to their volume fractions, the modulus is given by:

$$E_{cL} = E_r \, . \, \upsilon_r + E_m \, . \, \upsilon_m \qquad (IV.4)$$

Where:

ε_{cL} = longitudinal modulus of the composite

E_r, E_m = module of the reinforcement and matrix, respectively.

This relationship provides a first approximation of the mechanical behavior of unidirectional composites under tensile loading and is widely used in composite design and material selection.

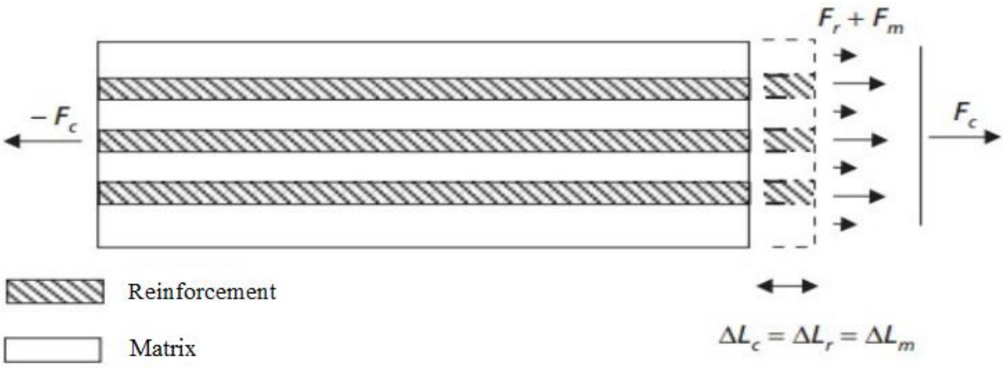


Figure IV. 2 : Unidirectional fiber-reinforced composite bar under longitudinal loading.

Similarly, in the case of elastic deformation under loading perpendicular to the plane of reinforcement (i.e., transverse to the fiber direction), the strains add, while the stresses remain equal in both the matrix and reinforcement phases.

In this configuration, the inverse of the Young's module obeys the rule of mixtures. This means that the transverse modulus of the composite is calculated using the following relationship:

$$\frac{1}{E_c} = \left(\frac{1}{E_r}\right) \sqrt{\upsilon_r} + \left(\frac{1}{E_M}\right) . \left(1 - \sqrt{\upsilon_m}\right) \qquad (IV.5)$$

This formula better accounts for the geometry and distribution of fibers, particularly when the reinforcement is in the form of long or short fibers rather than continuous sheets.

Similarly, for the transverse Poisson's ratio under longitudinal tensile loading, the effective value can be estimated using the rule of mixtures:

$$\frac{1}{E_c} = \left(\frac{1}{E_r}\right) + \left(\frac{1}{E_M}\right) .(1 -) \qquad (IV.6)$$

This relationship is strictly valid only when the reinforcements are in the form of continuous plates. In the case of fibers, a more accurate formula for the transverse Young’s modulus of the composite is given by:

$$\nu_{cLT} = \nu_r \, . \, V_r + V_m \, , \, \nu_m \qquad (IV.7)$$

Where:

ν_{cLT}: Poisson’s ratio of the composite in the longitudinal-transverse direction

ν_r, ν_m : Poisson’s ratios of the reinforcement and matrix

ν_r , ν_m : Volume fractions of the reinforcement and matrix

The elastic limit of the composite in the fiber direction, denoted R_{ec} , can be estimated using a rule of mixtures approach:

$$R_{ec} = R_{er} \, . \, \nu_r + R_{em} \, . \, \nu_m \qquad (IV.8)$$

Where:

R_{ec} : Elastic limit of the composite in the fiber direction

R_{er}, R_{em} : Elastic limits of the reinforcement and matrix, respectively

ν_r, ν_m : Volume fractions of the reinforcement and matrix

This equation assumes that both phases deform elastically up to failure and that perfect bonding exists at the interface.

The ultimate tensile strength of the composite in the fiber direction, denoted R_{mc} , is similarly given by:

$$R_{mc} = R_{mr} \, . \, \nu_r + R_{mm} \, . \, \nu_m \qquad (IV.9)$$

Where:

R_{mc}= Tensile strength of the composite

R_{mr} , R_{mm} : Tensile strengths of the reinforcement and matrix

This formulation reflects the contribution of each constituent to the composite's overall strength, weighted by their respective volume fractions. However, in practice, the failure mode often depends on the matrix–fiber interface behavior and may deviate from the idealized prediction.

IV.4. Processing Techniques

IV.4.1 Manual Fabrication Methods

a) Hand Lay-Up (Contact Molding)

The hand lay-up process, also known as contact molding, is a versatile method used to manufacture composite parts of various sizes and geometries, whether simple or complex. This process is particularly well-suited for the fabrication of molds, prototypes, and for repair work.

It requires minimal equipment and tooling, making it cost-effective for low to medium production volumes, typically ranging from 500 to 800 parts per mold per year. Layers of reinforcement (e.g., fiberglass mats) are manually placed in a mold and impregnated with a thermosetting resin (such as polyester or epoxy), often with the aid of brushes or rollers to ensure full wetting and air removal.

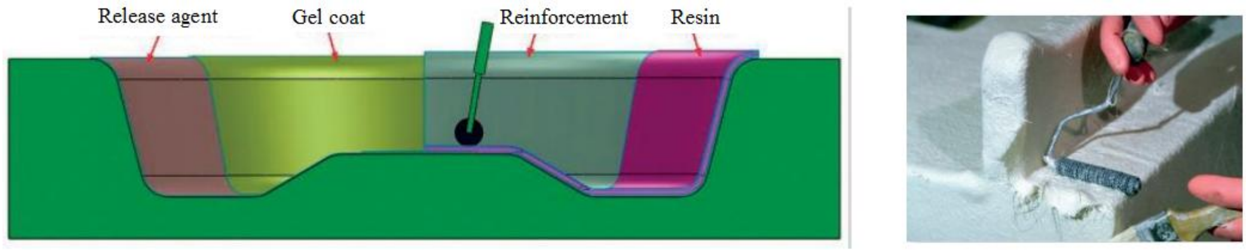


Figure IV. 3 : The hand lay-up process.

b) Simultaneous Spraying Process

The simultaneous spraying process is a semi-mechanized manufacturing method used to produce large composite parts with simple or complex geometries. It is a fast and user-friendly technique, particularly suitable for medium to large-scale production.

This process employs a spray machine equipped with a chopper gun, which simultaneously:

- Chops continuous fiber rovings (usually glass),
- Impregnates them with resin, and
- Spray the resin-fiber mixture directly onto the mold surface.

Simultaneous spraying ensures good material distribution, reduces labor effort compared to manual lay-up, and is widely used in industries such as transportation, marine, construction, and sanitary products, where structural performance with simplified fabrication is required.

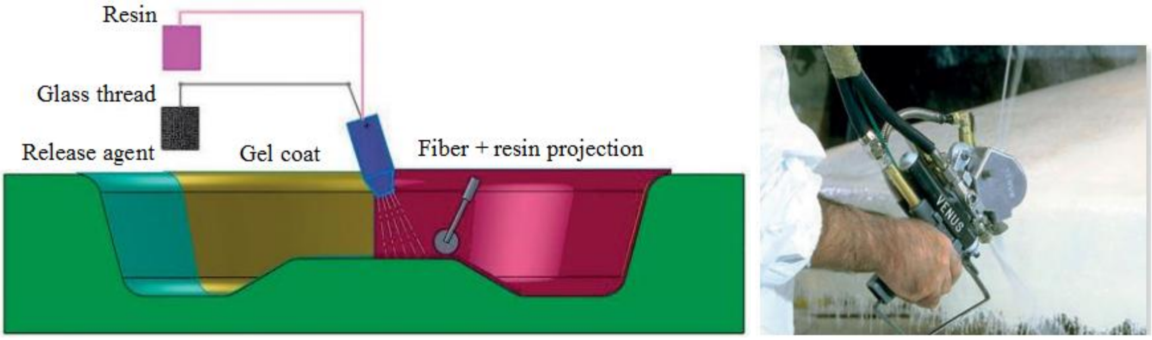


Figure IV. 4 : Simultaneous Spraying Process.

c) Medium-Series Manufacturing Processes

Low-Pressure Injection Molding (RTM – Resin Transfer Molding)

Resin Transfer Molding (RTM) is a semi-automated closed-mold process used to manufacture composite parts with low to medium geometric complexity and surface areas typically under 6m². In RTM, dry reinforcements (e.g., fiberglass mats or fabrics) are placed into a closed rigid mold, after which a thermosetting resin (such as polyester or epoxy) is injected under low pressure to impregnate the fibers. The mold is then heated or cured at room temperature to solidify the part.

Parts produced using RTM have:

- Constant thickness,
- Two smooth surfaces, which may be gel-coated or uncoated depending on the application.

RTM offers excellent dimensional stability, surface finish, and fiber-to-resin ratio control, making it suitable for automotive, aerospace, and industrial components. Production rate varies from 1 to 3 parts per hour per mold, with annual outputs reaching up to 5000 parts per mold.

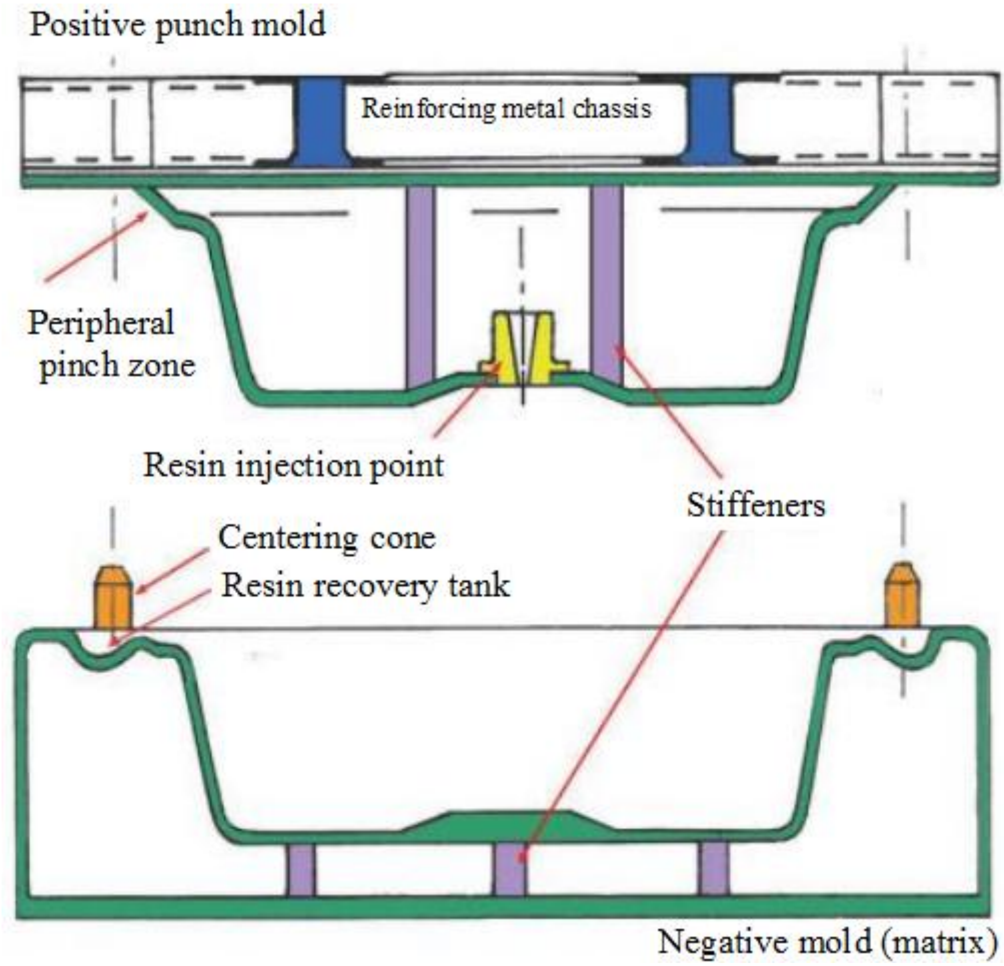


Figure IV. 5 : Medium-Series Manufacturing Processes.

Thermoforming

Thermoforming is a forming process in which a reinforced thermoplastic sheet is heated until softened and then shaped over a positive mold using vacuum suction to ensure it conforms precisely to the mold's surface.

This technique is widely used for producing lightweight components with simple or moderately complex geometries, and it is valued for its short cycle times, cost-efficiency, and compatibility with recyclable materials. The process is particularly suitable for medium-series production and is common in sectors such as automotive interiors, packaging, and sanitary equipment.

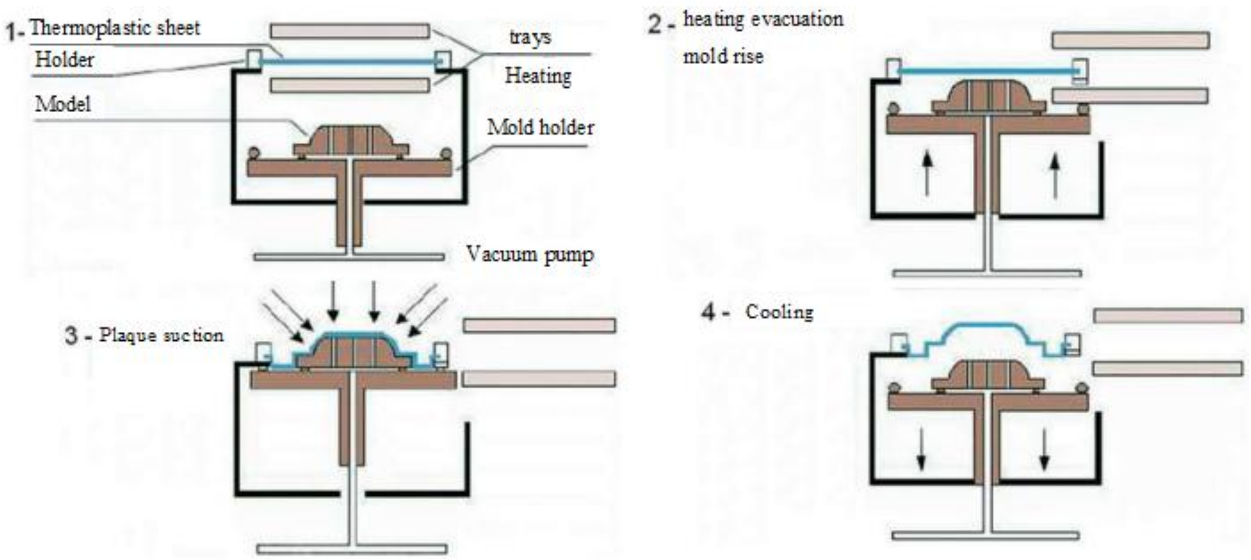


Figure IV. 6 : Thermoforming processes.

High-Volume Manufacturing Processes

Low-Pressure Cold Compression Molding (Wet Method)

Low-pressure cold compression molding, also referred to as the wet method, is a process used for mass production of composite parts. Operating at pressures typically below 5 bars, the method involves manually placing successive layers of reinforcement into a mold, which may or may not be pre-coated with gelcoat.

Once the reinforcements are positioned, a measured quantity of thermosetting resin is applied, and the stack is compressed to ensure full impregnation of the fibers.

The curing (hardening) of the composite may occur at room temperature or be accelerated by applying heat, depending on the type of resin system used.

This process is particularly suitable for:

- Producing parts with constant thickness,
- Smooth surface finish, and
- High production rates, often used in the automotive, sanitary, and consumer goods industries.

Figure IV. 7 : Low-Pressure Cold Compression Molding (Wet Method).

High-Pressure Compression Molding of Compounds (SMC, BMC, etc.)

Compression molding at high pressure (HP) is a widely used industrial process for producing large volumes of composite parts with consistent quality and high production rates. It uses pre-formulated semi-finished products called compounds, which require no mixing or ingredient dosing prior to molding.

These compounds are typically based on polyester or vinyl ester resins, reinforced with glass or carbon fibers, and are available in two main forms:

- **Sheet Molding Compounds (SMC):**

Supplied as chemically thickened sheets, SMCs contain 20–35% chopped fibers (typically 2.5 to 5 cm long) and are ideal for compression molding of flat or moderately contoured parts. They offer good mechanical properties and surface finish.

- **Bulk Molding Compounds (BMC):**

Presented as a chemically thickened, dough-like bulk material, BMCs include 15–25% short glass fibers (3 to 12 mm in length). BMCs are particularly suited for the molding of complex geometries, electrical housings, and automotive components.

Both SMC and BMC can be shaped using heated metal molds under pressures ranging from 50 to 100 bars, producing parts with excellent dimensional accuracy, good surface quality, and short cycle times, making them ideal for mass production in the automotive, electrical, and appliance industries.

Pultrusion Molding

Pultrusion is a fully mechanized continuous molding process used to manufacture constant cross-section profiles with simple to moderately complex shapes. This process is particularly efficient for producing long, straight, and fiber-reinforced structural components.

In pultrusion:

- Continuous fiber reinforcements (rovings or mats) are impregnated with a thermosetting resin (such as polyester, epoxy, or vinyl ester) as they pass through an impregnation bath.
- The wetted fibers are then pulled through a heated die (typically ~1 meter long), maintained at 100–120 °C, which shapes and initiates the polymerization (curing) of the composite.
- The cured profile exits the die as a rigid, finished part and is subsequently cut to the desired length.

This process ensures high fiber content, excellent mechanical performance, and high production speed, making it ideal for manufacturing:

- Structural profiles (rods, beams, channels),
- Ladder rails, cable trays, window frames,
- And components used in construction, electrical, and marine sectors.

Figure IV. 8 : Pultrusion Molding

IV.4. Damage in Composite Materials

IV.4.1 Internal defects

The primary forms of degradation in fiber-reinforced composite materials are caused by mechanical loading. Due to the structured network of interfaces in laminated composites particularly those reinforced with long fibers these materials are especially vulnerable to damage. This vulnerability stems from the presence of interfaces between constituents with significantly different mechanical properties, such as stiff fibers embedded in a more compliant matrix.

Under applied stress, damage tends to propagate along the fiber paths, but the nature of the damage also depends on the direction of loading relative to the fiber orientation. Different failure mechanisms may occur depending on whether the load is parallel or transverse to the fibers, or within the interlaminar plane.

The main types of damage in composite materials include:

a) Fiber Breakage:

Occurs when the tensile stress exceeds the fiber's ultimate strength, leading to local failure that can trigger further degradation.

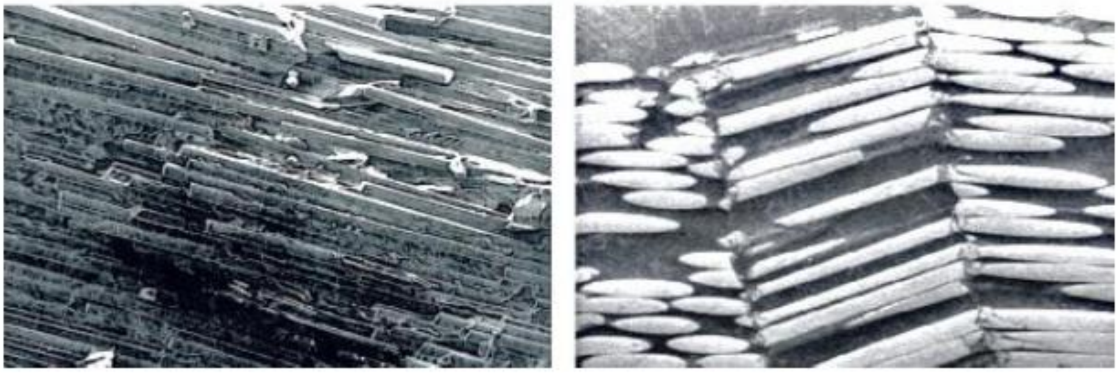


Figure IV. 9 : Fiber Breakage

b) Fiber–Matrix Debonding:

This interfacial failure results from poor adhesion or stress concentration, leading to loss of load transfer efficiency between the fiber and the surrounding matrix.

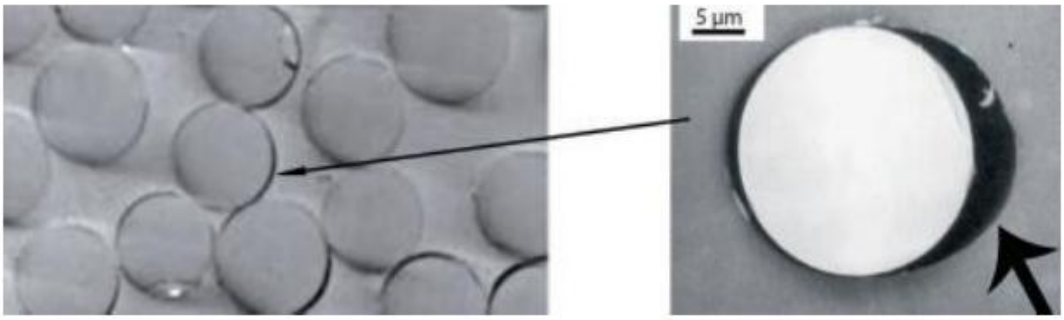


Figure IV. 10 : Fiber–Matrix Debonding

c) Intra-ply Damage:

Refers to microcracks and fiber kinking within individual plies, typically due to compressive or transverse loads.

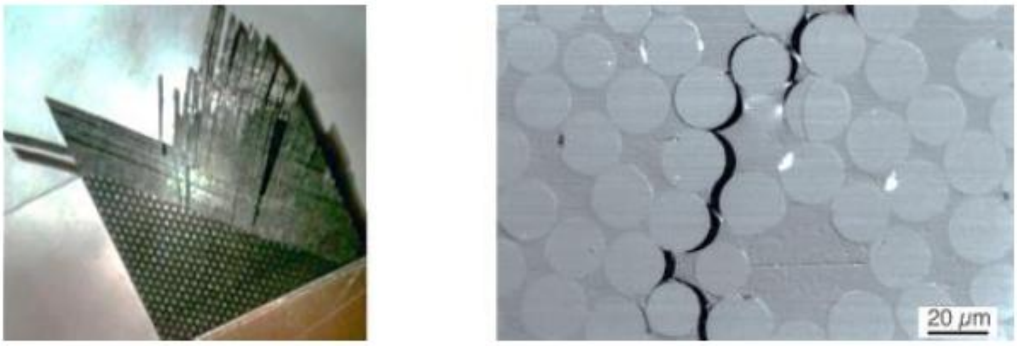


Figure IV. 11 : Defect with intra-ply Damage

d) Delamination:

The separation between adjacent plies (layers) of the laminate, often initiated by impact, cyclic loading, or through-thickness stress. It significantly compromises structural integrity and may propagate under continued loading.

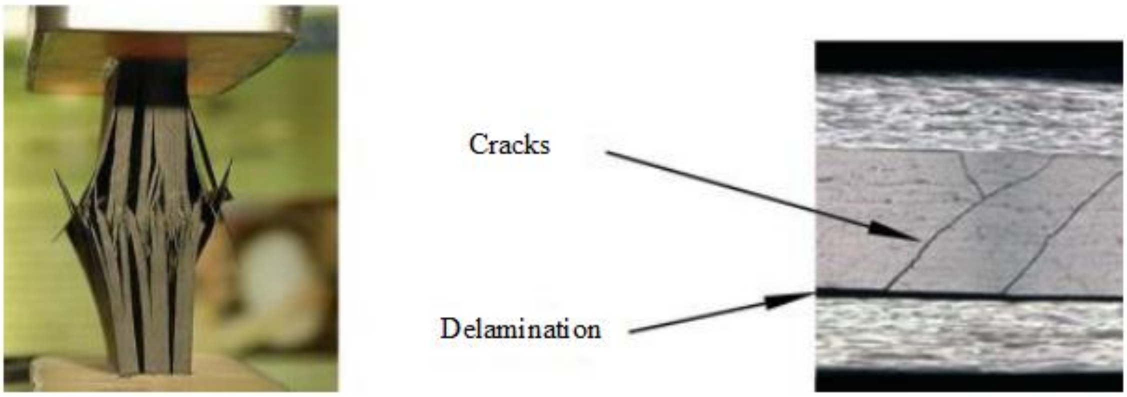


Figure IV. 12 : Defect with delamination

IV.4.2 Surface Defects in Composite Materials

Surface quality is a key criterion in the performance and appearance of composite parts. Several types of surface defects may arise during manufacturing or curing, affecting not only the aesthetics but also the mechanical integrity of the final product. The most common surface defects include:

a) Shrinkage:

Caused by resin volume contraction during curing, shrinkage leads to surface waviness, print-through, or dimensional inaccuracies, especially in thin sections or near sharp transitions.

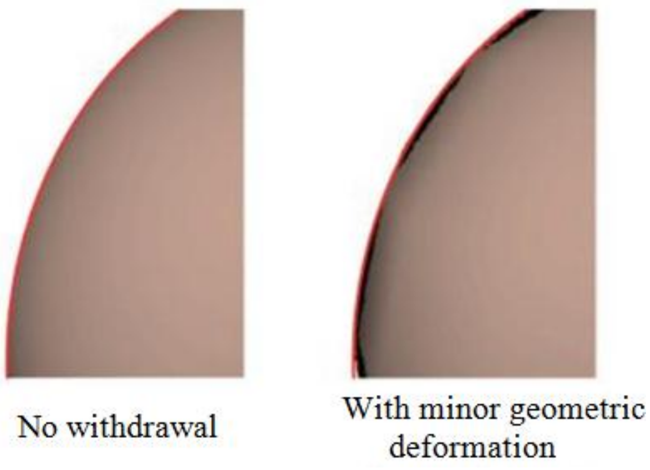


Figure IV. 13 : Defect with shrinkage

b) **Porosity:**

The presence of air bubbles or voids trapped within the resin matrix or at the fiber interface. Porosity typically results from incomplete impregnation, excessive curing speed, or insufficient vacuum or pressure. It reduces the mechanical strength and can act as initiation sites for cracks.

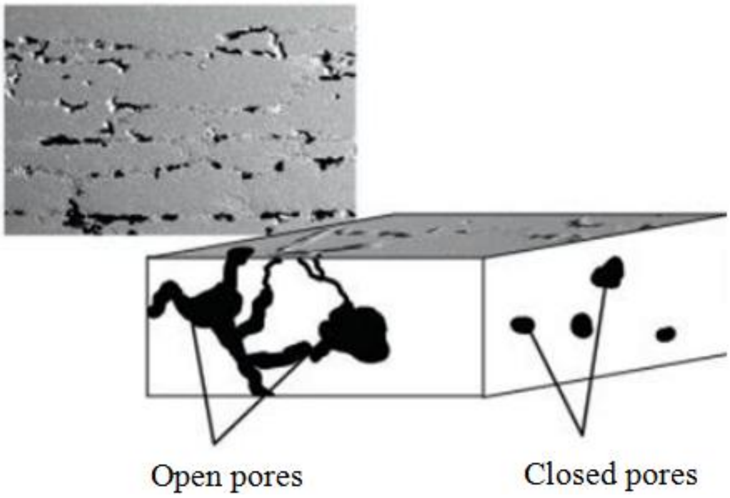


Figure IV. 14 : Defect with porosity

c) **Chipping or Flaking :**

This defect appears as localized surface detachment or flaking, often caused by poor adhesion between the matrix and surface coatings or by impact, thermal cycling, or environmental exposure.

Figure IV. 15 : Defect with chipping.

d) Waviness / Telegraphing:

Also known as "print-through", this phenomenon occurs when the underlying fiber pattern becomes visible on the surface. It is often due to uneven curing, excessive shrinkage, or inconsistent gelcoat thickness, and is more noticeable on thin laminates or high-gloss finishes.

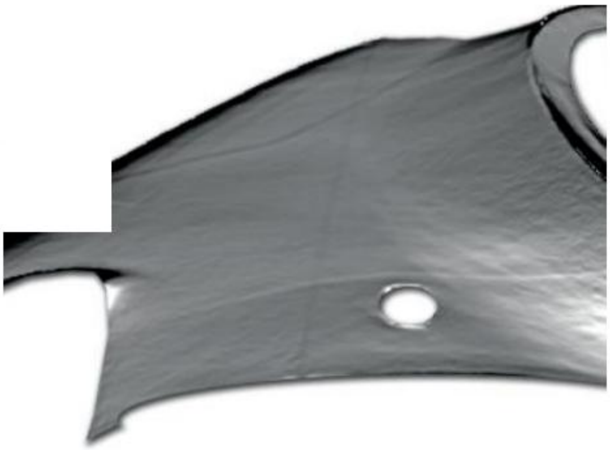


Figure IV. 16 : Defect with waviness.

IV.5 Failure Criteria

Failure criteria (or strength criteria) are macroscopic characteristics of materials that are determined through a minimal number of mechanical tests. These criteria serve as essential tools for engineers in evaluating the mechanical resistance of a structure under a specific loading configuration, which often differs from the standard conditions used during material characterization tests.

In its broadest definition, mechanical strength refers to the ultimate stress (i.e., the maximum stress the material can sustain before rupture), or the stress level at which irreversible damage occurs, indicating the end of elastic behavior.

For isotropic materials (materials with uniform properties in all directions), the ultimate strength under tensile, compressive, or shear loading can be treated without reference to orientation. In the case of ductile isotropic materials, a well-known and effective failure criterion is the von Mises criterion, which uses a single calibration parameter to predict yielding.

However, in the case of composite materials, such simplifications are no longer valid. The ultimate strength of a unidirectional composite is highly dependent on both the direction and type of the applied load (tensile or compressive, along or across fibers). As such, any failure criterion suitable for composites must incorporate multiple adjustable parameters to accurately account for anisotropic behavior, different damage modes, and directional dependence of mechanical response.

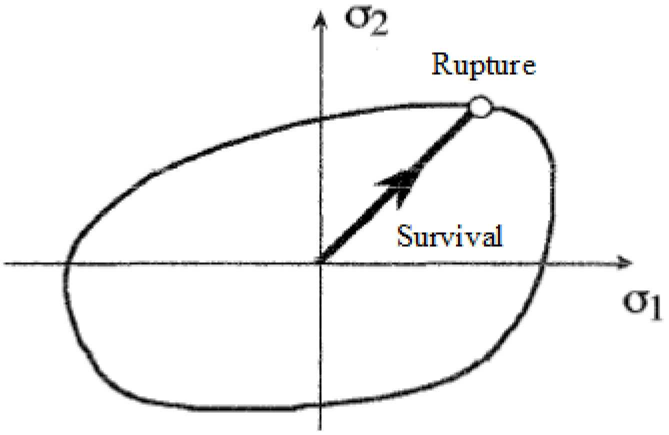


Figure. IV.17: Limit criterion in the σ_1–σ_2 stress plane

IV.5.1 Failure Surface and Criterion Representation

A failure criterion can be represented as a closed surface in the space of stresses or strains. Under the assumption of plane stress, the criterion is often visualized as a tri-rectangular diagram in the space defined by σ_1, σ_2 and σ_6 (or equivalently, ε_1, ε_2 and ε_6 for strain-based approaches).

If the loading state, represented as a point in this space (typically multiaxial), lies inside the failure surface, the material is considered to remain undamaged. Failure occurs when the representative point reaches the boundary of the surface. The analytical expression of this surface the failure criterion is selected to best match experimental observations and is calibrated using a minimum number of mechanical tests, ideally those that are simple to perform.

Numerous failure criteria have been proposed for composite materials, owing to their anisotropy and complex failure mechanisms. In the following sections, we will describe several widely used criteria:

- Maximum stress criterion
- Maximum strain criterion
- Interactive criteria, such as:
- Von Mises (for isotropic ductile materials),
- Hill's criterion, and
- Tsai-Wu criterion (for anisotropic composites)

IV.5.2 Von Mises Criterion

The Von Mises criterion is applicable to isotropic and ductile materials, where plastic deformation occurs primarily through shear slip along planes oriented at 45° to the principal stress directions. This criterion is based on a limiting value of the octahedral shear stress, which is mathematically equivalent to considering a maximum energy of distortion per unit volume stored in the material.

This energy-based approach provides a scalar measure of the multiaxial stress state, and yielding is predicted to occur when the distortion energy reaches a critical value, independent of hydrostatic stress. It is widely used in metal plasticity and serves as a benchmark for understanding more complex composite failure models.

$$1/2\,[(\sigma_I - \sigma_{II})^2 + (\sigma_{II} - \sigma_{III})^2 + (\sigma_{III} - \sigma_I)^2] = K \qquad (\mathrm{IV.}\,10)$$

The parameter k is determined by a tensile test ($\sigma_I \neq 0$, $\sigma_i = 0$, i =2 to 6). The limit value being X; we then have:

$$2X^2 = 9K \qquad (\mathrm{IV.11})$$

The shear resistance S (only $\sigma_I \neq 0$) is then given by:

$$3S^2 = X^2 \qquad (\mathrm{IV.12})$$

This criterion is even; it leads to the same limits in tension and compression.

For plane stresses, the von Misses criterion is written:

$$\sigma_1^2 + \sigma_{22}^2 - \sigma_1\sigma_2 + 3\sigma_6^2 = X^2 \qquad (\mathrm{IV.13})$$

IV.5.3 Maximum Stress Criterion

This criterion assumes that failure occurs when any of the principal stress components in the material exceeds its corresponding ultimate stress.

For a unidirectional composite material, failure is predicted when:

The composite is deemed unbroken if all of the following inequalities are true:

unbroken if:

$$\begin{aligned} -X' &< \sigma_X < X \\ -Y' &< \sigma_Y < Y \\ -S &< \sigma_S < S \end{aligned} \tag{IV.14}$$

Conversely, the material is broken if one of the following equalities is reached, as the load increases:

broken if :

$$\begin{aligned} &\sigma_X = -X \text{ ou } \sigma_X = X \\ &\text{ou } \sigma_Y = -Y \text{ ou } \sigma_Y = Y \\ &\text{ou } \sigma_S = -S \text{ ou } \sigma_S = S \end{aligned} \tag{IV.15}$$

The boundary surface is a rectangular parallelepiped in the frame σ_X, σ_Y, σ_S

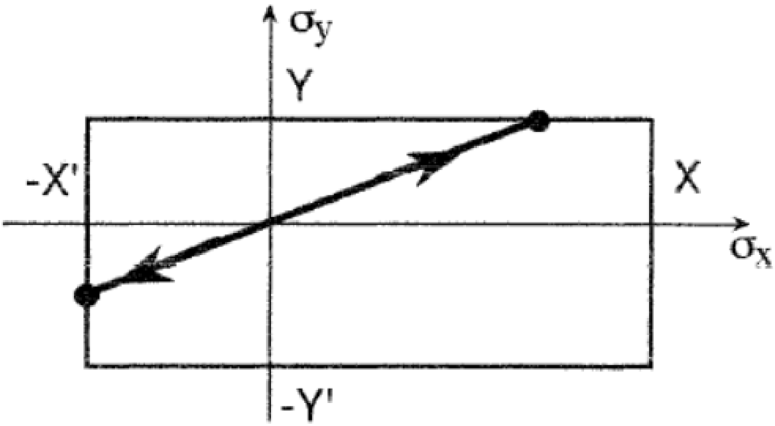


Figure. IV.18 : Maximum stress criterion represented in the σ_X, σ_Y plane.

IV.5.4 Maximum Strain Criterion

This criterion is similar to the previous one, but uses strain limits instead of stress:

$$\begin{aligned} -\frac{X'}{E_X} &< \varepsilon_X < -\frac{X}{E_X} \\ \frac{Y'}{E_Y} &< \varepsilon_Y < -\frac{Y}{E_Y} \\ \frac{S}{E_S} &< \varepsilon_S < -\frac{S}{E_S} \end{aligned} \tag{IV. 16}$$

The maximum strain criterion is also represented by a rectangular parallelepiped, but in the ε x , εy, εs diagram.

It can also be represented in stress space, as shown schematically below in the σ_X, σ_Y plane:

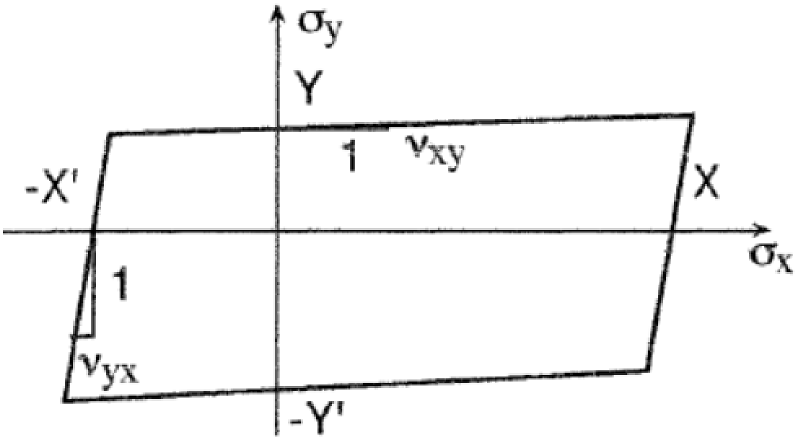


Fig. IV.7: Criterion of maximum deformation, given in the plane σ_X, σ_Y.

This approach is useful when the strain field is known, especially in finite element simulations. However, like the maximum stress criterion, it does not account for interactions between directions.

IV.5.6 Hill's Criterion (for anisotropic materials)

Hill extended the Von Mises criterion to handle orthotropic materials. It introduces different constants to account for anisotropy in strength:

Where:

$$F(\sigma_1 - \sigma_2)^2 + G(\sigma_2 - \sigma_3)^2 + H(\sigma_3 - \sigma_1)^2 + 2L\sigma_4^2 + M\sigma_5^2 + 2N\sigma_6^2 = K \quad \text{(IV.17)}$$

F,G,H,L,M,N: Material-dependent constants, determined experimentally.

Hill's criterion is often used in sheet metal forming, but has also been adapted for certain composite applications with moderate anisotropy.

IV.5.7 Tsai-Wu Criterion (for composite materials)

This is a fully interactive polynomial failure criterion widely used in composite material design. It combines linear and quadratic stress terms:

$$F_{ij}\, \sigma_i\, \sigma_j + Fi\, \sigma_i = 1 \quad \text{(IV.18)}$$

σ_i : Stress components

$F_{ij,}$ Fi : Material strength coefficients (obtained from experiments)

or strains :

$$G_{ij}\, \varepsilon_i\, \varepsilon_j + Gi\, \varepsilon_i = 1 \quad \text{(IV.19)}$$

The Tsai-Wu criterion allows for interaction between different stress components and can distinguish between tensile and compressive strength. It is considered one of the most comprehensive and realistic criteria for anisotropic, fiber-reinforced composites.

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