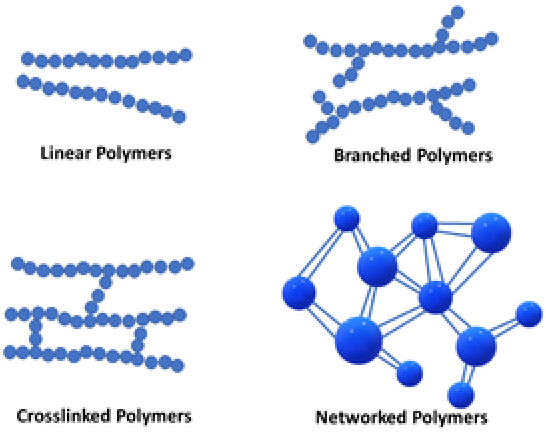
A236

Polymer (matrix) structure
Foundational knowledge article



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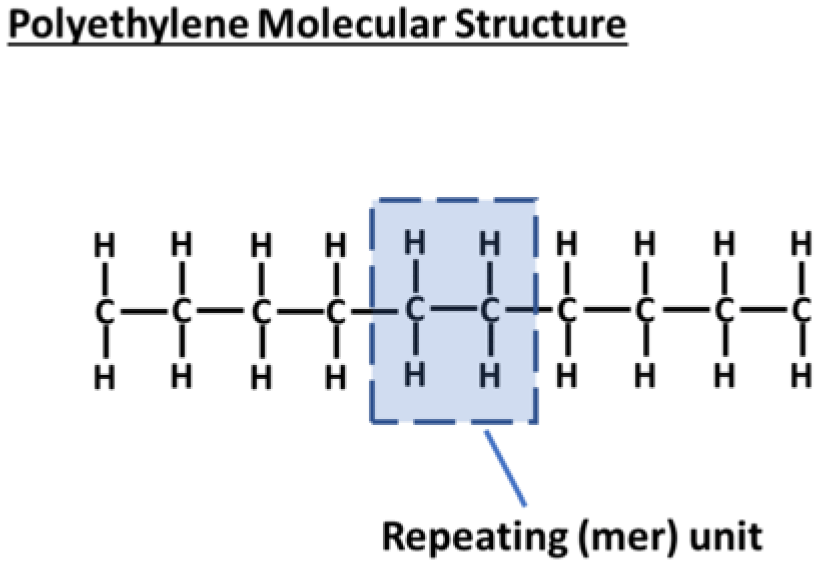
Overview[edit | edit source]

Polymer materials have molecular structures with long chains comprised of small repeating units. The origin of the word **polymer** comes from the Greek words **poly** (many) and **meros** (part) [1]. Many engineering polymer materials are organic compounds chemically based on carbon, hydrogen, and other non-metallic compounds. Polymers are characteristically low in density and flexible compared to the other material classes [2].

For polymer matrix composites (PMC), both thermoset or thermoset polymers can be used as the matrix. The choice of matrix polymer material determines both the composite’s environmental resistance and maximum service temperature.

Polymer Molecular Structure[edit | edit source]

Polymers are comprised of long molecules that are made up of smaller repeating units (also known as a "mer") joined together end to end. Illustrated below is the simple example of polyethylene (PE), with its repeating molecular structure.



Molecular composition of polyethelene (PE) polymer chain structure.

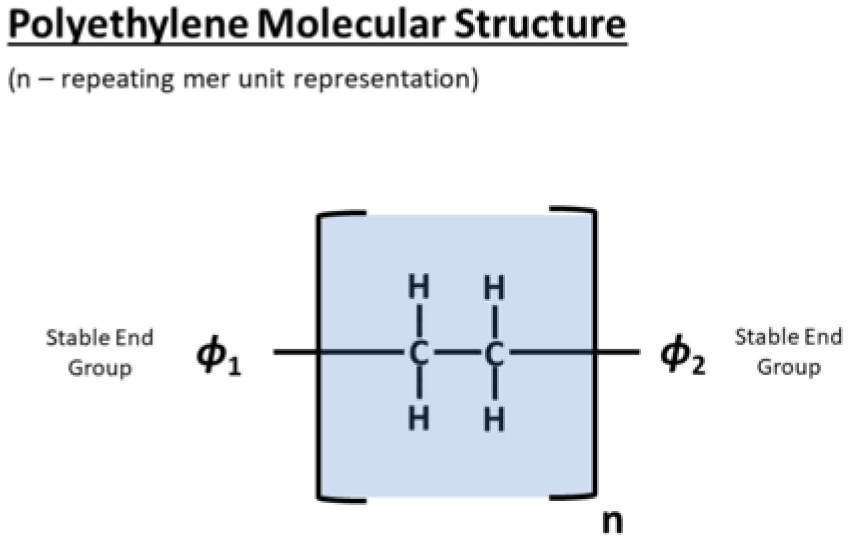
As more repeating molecular units are added, the polyethylene molecular chain length grows and extends, and its molecular weight increases (more precisely molecular mass or molar mass – but it is commonly referred to as molecular weight in the polymer literature).

The mechanical properties exhibited by the polymer are dependent on two molecular factors:

1. The length of the molecule
2. The shape, i.e. configuration, of the molecule

Molecular Length[edit | edit source]

The joining of the repeating molecular units creates a chain-like molecular structure for the polymer. Polymers with very long chains feature extremely large molecular weight [2]. Not all the polymer chains grow to the same length – as a result, the average molecular weight or the average number of repeat units in a chain is typically reported for the polymer.



Polyethylene (n repeating units) representation of molecular polymer chain. n - repeating molecular units, ϕ - stable end groups.

As the number of repeating units (n) increases, both the physical polymer chain length and the corresponding molecular weight of the polymer increases.

Molecular Configuration[edit | edit source]

There are several molecular configurations that can be observed for polymers. The basic configurations are as follows.

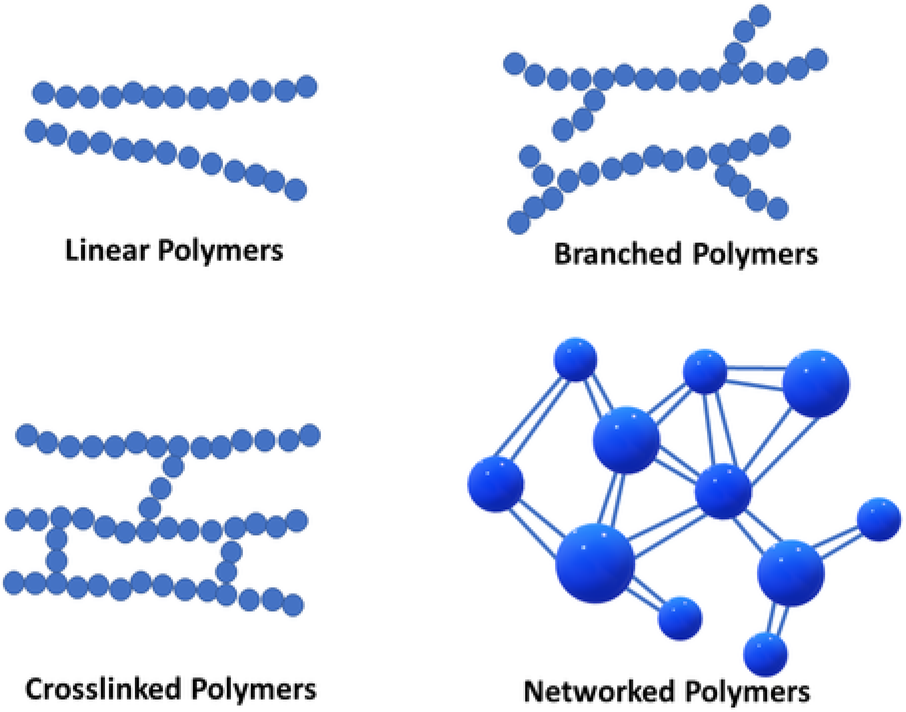


Illustration of the various polymer chain configurations observed in polymers. The illustrated circles represent the repeating molecular units.

Linear Polymer

Linear polymers consist of long chain-like structures where repeating units are joined together end to end. The long linear chains are flexible, where van der Waals and hydrogen bonding may occur between polymer chains while in close proximity – leading to chain entanglement.

Branched Polymers

Branched polymers feature short side branched chains that are connected to the main (longer) polymer chains. The packing efficiency of the polymer with side branching is reduced, lowering the polymer density.

Crosslinked Polymers

The linear polymer chains of crosslinked polymers are joined together via covalent bonding of smaller molecules acting as bridges between them. The crosslinking process often takes place through a non-reversible chemical reaction process (curing). Crosslink formation characterizes thermoset polymers.

Networked Polymers

Networked polymers feature mer units with three active covalent bonds, and have the ability to form interconnected three-dimensional network configurations [2]. Networked polymers include highly crosslinked polymers. For example, highly crosslinked epoxies are often described to have a highly crosslinked three-dimensional epoxy network configuration.

Microstructure[edit | edit source]

Polymers can exhibit two basic morphologies (structures), or a combination of the two, when “frozen” in their solid state. These basic morphologies are illustrated below.

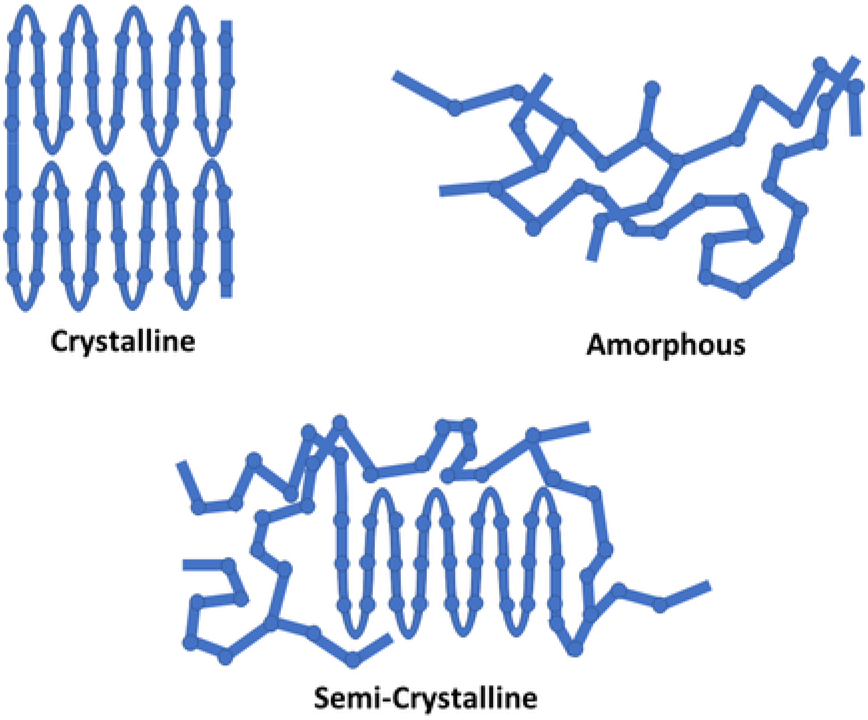


Illustration of the basic polymer morphology structures: crystalline (repeating arrays of densely packed folded structure regions), amorphous (without structure), and semi-crystalline (combination of both crystalline and amorphous structure regions).

Crystalline	Amorphous	Semi-Crystalline
• Periodic 3-D repeating array of molecules • Folded up into densely packed regions called crystals	• Literally without structure • No repeating array • Randomly coiled	• Both regions of crystalline and amorphous molecular arrangements

Common observed microstructures[edit | edit source]

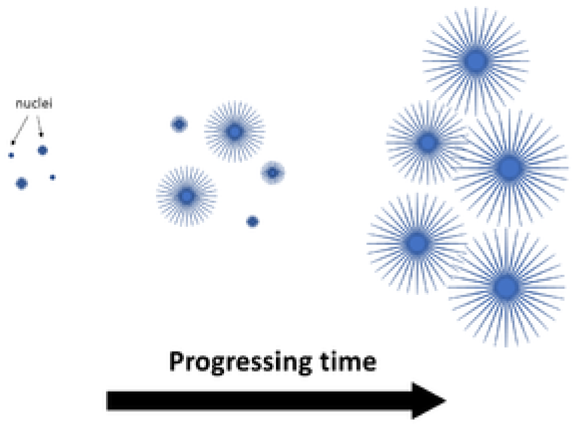


Illustration of spherulite crystal structures and their growth with time when cooled below the polymer melting temperature (Tm).

Thermoset polymers are generally amorphous in microstructure – a consequence of the lack of chain mobility that results from crosslinking. The polymer chains do not have the physical ability to re-organize into packed and folded molecular chain structures.

Thermoplastic polymers on the other hand typically exhibit a combination of both amorphous and crystalline regions, forming a semi-crystalline microstructure. The crystalline structures often take the form of spherulites – which form in a polymer that is cooled from its melted molten state back to a solid.

Initially starting as nuclei appearing in a super cooled polymer melt (below melting temperature Tm), the spherulite structures grow outward in the radius direction with progressing time. Spherulite growth is actually the growth of many smaller crystals forming the larger structure [1]. As the spherulites grow, polymer becomes trapped between these structures – the amorphous polymer regions.

Thermoset Polymers[edit | edit source]

Link to main Thermoset polymers page

Thermoset or thermosetting polymers are characterized by the molecular crosslink network of covalent bonds that are formed between adjacent primary polymer chains. Thermosets undergo polymerization and crosslinking during a curing stage with the aid of a hardening agent and heating or promoter.

During curing, they change from viscous fluid to rubbery gel (viscoelastic material) and finally glassy solid. If heated after curing, initially they become soft and rubbery at high temperatures. If further heated, they do not melt but decompose (burn). Thermoset polymers effectively become irreversibly hardened after curing and cannot be reprocessed, making them single use and not recyclable.

Popular examples of thermoset polymers include epoxy and polyester.

Thermoplastic Polymers[edit | edit source]

Link to main Thermoplastic polymers page

A class of polymer that is characterized to have the ability to flow when heated. Typically linear or branched in structure, upon heating, thermoplastics soften and melt where they flow in a manner of a viscous liquid. This process is repeatable upon repeated heating and cooling, making them potentially recyclable.

The high viscosity of thermoplastics when melted, make it difficult to saturate fibers in the composite manufacturing process. A lot of pressure and heat are required to process.

Some common examples of popular thermoplastics include polypropylene and polyethylene.

Explore this area further

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    - Thermoplastic polymers - A161
    - Thermoset polymers - A105

References

1. ↑ 1.0 1.1 [Ref] McCrum, N. G. et al. (1997). *Principles of Polymer Engineering*. Oxford University Press. ISBN 978-0-198565-26-0.
2. ↑ 2.0 2.1 2.2 [Ref] Callister, William D. (2003). *Materials Science and Engineering: An Introduction*. John Wiley & Sons, Inc. ISBN 0-471-13576-3.

About **Help**

The continuous material phase that binds the reinforcement together, maintains shape, transfers load, protects the reinforcement from environment and damage, and provides the composite support in compression.

Desirable characteristics:

- Moisture/chemical resistance
- Low density
- Processability

Polymer Matrix Composites (PMC).

Thermosets are a class of polymer that undergo polymerization and crosslinking during curing with the aid of a hardening agent and heating or promoter. Initially they behave like a viscous fluid. During curing, they change from viscous fluid to rubbery gel (viscoelastic material) and finally glassy solid.

If heated after curing, initially they become soft and rubbery at high temperatures. If further heated, they do not melt but decompose (burn)

Comes in two parts: part A (resin) and B (hardener). When mixed, curing reaction starts and is not reversible.

Examples include epoxy or polyester.

Engineered materials (designed to have specific properties) made from two or more constituent materials with different physical or chemical properties. The constituents remain separate and distinct on a macroscopic level within the finished structure.

Periodic 3-D, repeating array of molecules.

Literally "without structure", randomly coiled molecular polymer chains.

A portion of the molecular polymer chains tend to ‘fold up’ into densely packed regions called crystals.

In composites processing, viscosity is an indicator of how easily the resin matrix will mix with the reinforcement and how well it will stay in place during processing. The lower the viscosity, the more easily resin flows. Resin viscosity ranges considerably across chemistries and formulations.

By scientific definition, viscosity is a measure of a material’s resistance to deformation. For liquids, it is in response to imposed shear stresses.