

10: POLYMERS



CHAPTER OVERVIEW

10: Polymers

- 10.1: Polymerization - Making Big Ones Out of Little Ones
- 10.2: Polyethylene - From the Battle of Britain to Bread Bags
- 10.3: Addition Polymerization - One + One + One + ... Gives One!
- 10.4: Rubber and Other Elastomers
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- 10.6: Properties of Polymers
- 10.7: Plastics and the Environment

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10.1: Polymerization - Making Big Ones Out of Little Ones

Learning Objectives

- Define the terms *monomer* and *polymer*.
- Know the different types of natural polymers.

A **polymer** is a large molecule, or macromolecule, composed of many repeated subunits. The term "polymer" derives from the Greek word *polus* (meaning "many, much") and *meros* (meaning "part"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. As shown schematically in Figure 10.1.1.

Due to their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

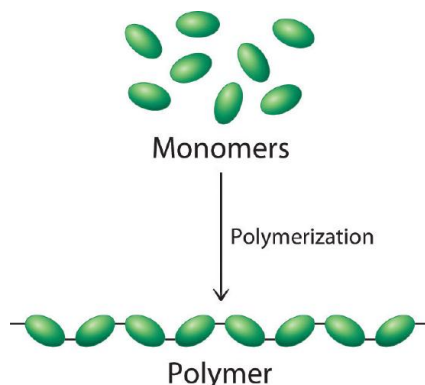
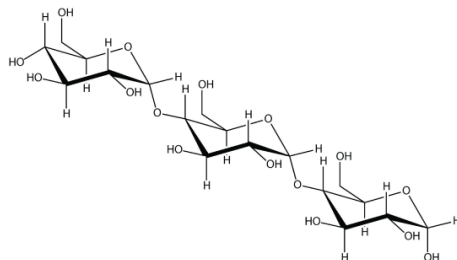


Figure 10.1.1 Polymer formation during a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.

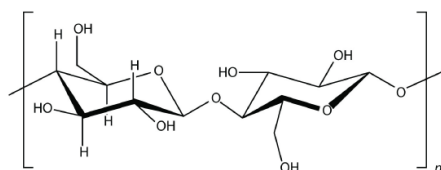
Natural Polymers

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. **Proteins** are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. Proteins play a crucial role in living organisms.

Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. **Cellulose** is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (Figure 10.1.2 - Nucleotides). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

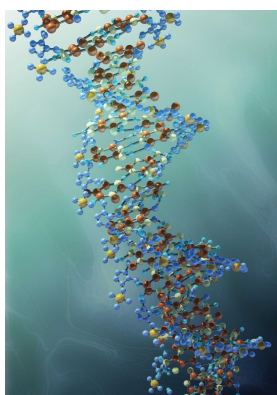


Figure 10.1.2 Nucleotides © Thinkstock

The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a N-containing base

The above mentioned biopolymers (polymers produced by living organisms) are discussed further in Chapter 16.

Celluloid: Billiard Balls

Celluloids are a class of compounds created from nitrocellulose (partially nitrated cellulose) and camphor, with added dyes and other agents. Generally considered the first thermoplastic, it was first created as Parkesinein (by Alexander Parkes of Birmingham England) in 1856 and as Xylonite in 1869. In the 1860s, an American, John Wesley Hyatt, acquired Parkes's patent and began experimenting with cellulose nitrate with the intention of manufacturing billiard balls, which until that time were made from ivory. In the 1870s the modified plastic was registered as "celluloid".

The main use was in movie and photography film industries, which used only celluloid film stock prior to the adoption of acetate safety film in the 1950s. Celluloid is highly flammable, difficult and expensive to produce and no longer widely used; its most common uses today are in table tennis balls, musical instruments, and guitar picks.

Bakelite (sometimes spelled **Baekelite**) or **polyoxybenzylmethyleneglycolanhydride** was the first plastic made from synthetic components. It is a thermosetting phenol formaldehyde resin, formed from a condensation reaction of phenol with formaldehyde. It was developed by the Belgian-American chemist Leo Baekeland in Yonkers, New York, in 1907.

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.



Video 10.1.2 Polymers Crash Course

Summary

- Polymers are giant molecules that consist of long chains of units called monomers connected by covalent bonds.
- Polymerization is the process of linking monomers together to form a polymer.
- Plastic is the general term for polymers made from synthetic materials.
- Several important biological polymers include proteins, starch, cellulose, DNA and RNA.

Contributors and Attributions

- Joshua Halpern, Scott Sinex and Scott Johnson
- TextMap: Beginning Chemistry (Ball et al.)
- [Marisa Alviar-Agnew \(Sacramento City College\)](#)
- Wikipedia

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10.2: Polyethylene - From the Battle of Britain to Bread Bags

Learning Objectives

- List the different types of polyethylene.
- Differentiate between thermolastic and thermosetting polymers.

Polyethylene was first synthesized by the German chemist Hans von Pechmann, who prepared it by accident in 1898. Industrial production of low-density polyethylene (LDPE) began in 1939 in England. Because polyethylene was found to have very low-loss properties at very high frequency radio waves, commercial distribution in Britain was suspended on the outbreak of World War II in order to produce insulation for UHF (ultra high frequency) and SHF (super high frequency) cables of radar sets.

Polyethylene or **polythene** is the most common plastic. As of 2017, over 100 million tonnes of polyethylene resins are produced annually, accounting for 34% of the total plastics market. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of n .

Polymers based on skeletons with only carbon are all synthetic. Let's begin by looking at polyethylene Figure 10.2.1. It is the simplest polymer, consisting of random-length (but generally very long) chains made up of two-carbon units.

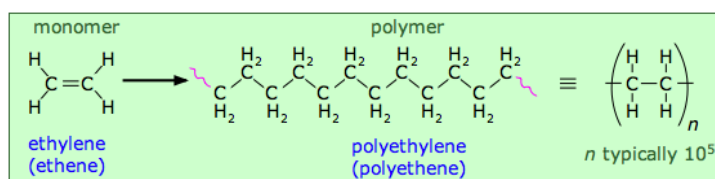


Figure 10.2.1 Polyethylene.

You will notice some "fuzziness" in the way that the polyethylene structures are represented above. The squiggly lines at the ends of the long structure indicate that the same pattern extends indefinitely. The more compact notation on the right shows the minimal repeating unit enclosed in brackets overprinted with a dash; this means the same thing and is the preferred way of depicting polymer structures.

Types of Polyethylene

Most of synthetic polymers are formed from ethylene. The relative lengths of the chains and any branches control the properties of polyethylene. The most important polymer grades with regard to volume are High density polyethylene (HDPE) Low density polyethylene (LDPE), and Linear low density polyethylene (LLDPE).

HDPE (High density polyethylene) is defined by a density of greater or equal to 0.941 g/cm^3 . HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE has high tensile strength. It is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes. One-third of all toys are manufactured from HDPE. In 2007, the global HDPE consumption reached a volume of more than 30 million tons.

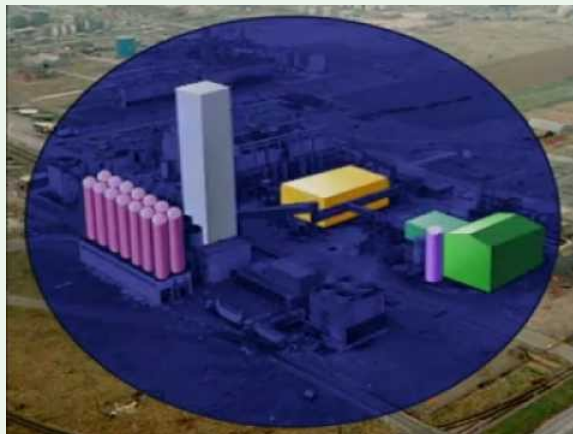
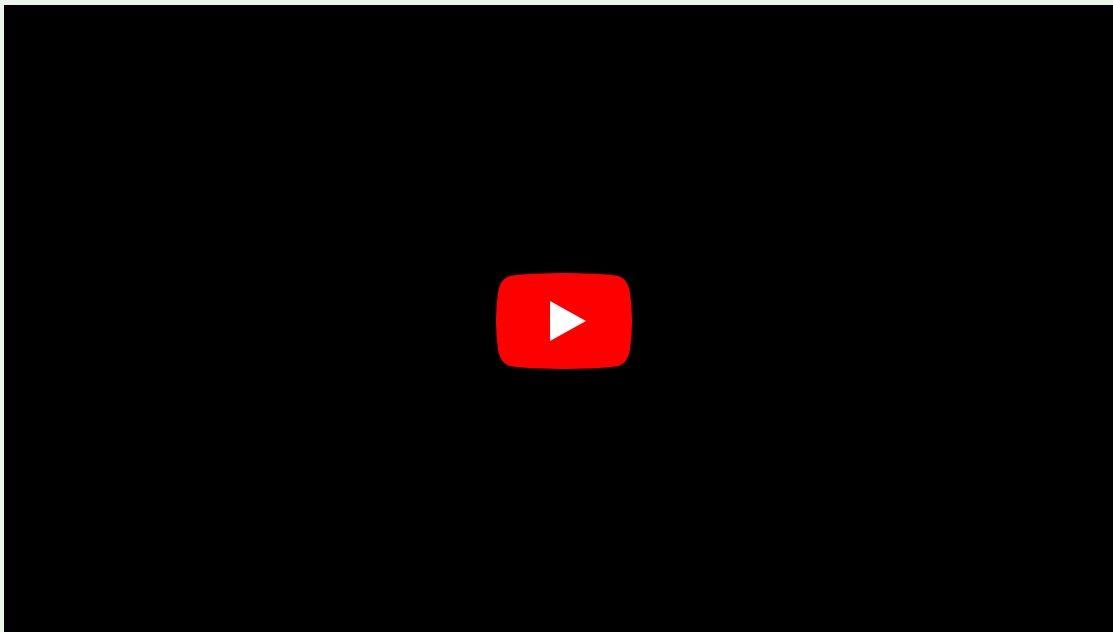
LDPE (Low density polyethylene) is defined by a density range of $0.910\text{--}0.940 \text{ g/cm}^3$. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market had a volume of almost US\$33 billion.

LLDPE (Linear low density polyethylene) is defined by a density range of $0.915\text{--}0.925 \text{ g/cm}^3$. LLDPE is a substantially linear polymer with significant numbers of short branches. LLDPE has higher tensile strength than LDPE, and it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress-cracking resistance, but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. It is used for cable coverings, toys, lids, buckets, containers, and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility, and relative

transparency. Product examples range from agricultural films, Saran wrap, and bubble wrap, to multilayer and composite films. In 2013, the world LLDPE market reached a volume of US\$40 billion.

Figure 10.2.2 A pill box presented to a technician at Imperial Chemical Industries (ICI) in Northwich, England in 1936 made from the first pound of polyethylene.

Polyethylene Production



Video 10.2.1 *The commercial production of Polyethylene (polyethene).* from the [Royal Society of Chemistry](#)

Thermoplastic and Thermosetting Polymers

Polymers can be classified by their physical response to heating. Polyethylene is a thermoplastic; however, it can become a thermoset plastic when modified (such as cross-linked polyethylene). **Thermoplastics** are plastics that soften when heated and become firm again when cooled. This is the more popular type of plastic because the heating and cooling may be repeated and the thermoplastic may be reformed.

Thermosets are plastics that soften when heated and can be molded, but harden permanently. They will decompose when reheated. An example is Bakelite, which is used in toasters, handles for pots and pans, dishes, electrical outlets and billiard balls.

Summary

Polyethylene is the long chain polymer formed from ethylene (ethene) monomers.

Polyethylene can be classified as HDPE, LDPE, and LLDPE based on how close the polymer chains pack together affecting its density.

Polymers can be classified as thermoplastics (can be reformed after repeated heating) or thermosets (harden permanently) based on their physical response to heating.

Contributors and Attributions

- Stephen Lower, Professor Emeritus ([Simon Fraser U.](#)) [Chem1 Virtual Textbook](#)
- Charles Ophardt, Professor Emeritus, Elmhurst College; Virtual Chembook
- Wikipedia

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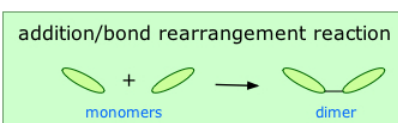
10.3: Addition Polymerization - One + One + One + ... Gives One!

Learning Objectives

- Define addition polymerization.
- Draw the structure of a polymer from its monomer.
- Know the uses/applications of common polymers.

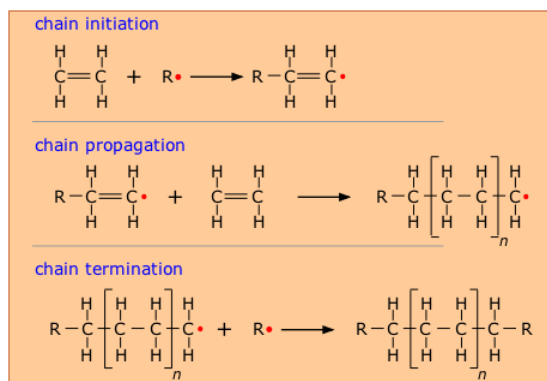
Addition polymerization and condensation polymerization are two modes of polymerization reactions in the formation of polymers. In addition polymerization, the monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any small molecules. Whereas, in condensation polymerization (Section 10.5) two different monomers combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers.

Addition or *chain-growth* polymerization involves the rearrangement of bonds within the monomer in such a way that the monomers link up directly with each other:



In order to make this happen, a chemically active molecule (called an *initiator*) is needed to start what is known as a *chain reaction*. The manufacture of polyethylene is a very common example of such a process. It employs a *free-radical* initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.

In theory, only a single chain-initiation process needs to take place, and the chain-propagation step then repeats itself indefinitely, but in practice multiple initiation steps are required, and eventually two radicals react (*chain termination*) to bring the polymerization to a halt.

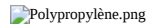


As with all polymerizations, chains having a range of molecular weights are produced, and this range can be altered by controlling the pressure and temperature of the process.

Polypropylene

Polypropylene (PP), also known as **polypropene**, is a thermoplastic polymer used in a wide variety of applications. It is produced via chain-growth polymerization from the monomer propylene. Phillips Petroleum chemists J. Paul Hogan and Robert Banks first polymerized propylene in 1951. Propylene was first polymerized to a crystalline isotactic polymer by Giulio Natta as well as by the German chemist Karl Rehn in March 1954. Polypropylene is used alone or as a copolymer, usually with ethylene. These polymers have an exceptionally wide range of uses — rope, binder covers, plastic bottles, staple yarns, non-woven fabrics, electric kettles. When uncolored, it is translucent but not transparent. Its resistance to fatigue makes it useful for food containers and their lids, and flip-top lids on bottled products such as ketchup.

After polyethylene, polypropylene is the most profitable plastic with revenues expected to exceed US\$145 billion by 2019. The sales of this material are forecast to grow at a rate of 5.8% per year until 2021. Polypropylene is produced by the chain-growth polymerization of propylene:

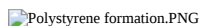


Polystyrene

Polystyrene was discovered in 1839 by Eduard Simon, an apothecary from Berlin. In 1941, Dow Chemical invented a Styrofoam process. Polystyrene is transparent but rather brittle, and yellows under uv light. Widely used for inexpensive packaging materials and "take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.

Expanded polystyrene (EPS) is a rigid and tough, closed-cell foam with a normal density range of 11 to 32 kg/m³. It is usually white and made of pre-expanded polystyrene beads. EPS is used for food containers, molded sheets for building insulation, and packing material either as solid blocks formed to accommodate the item being protected or as loose-fill "peanuts" cushioning fragile items inside boxes. EPS is colloquially called "styrofoam" in the United States and Canada, an incorrectly applied genericization of Dow Chemical's brand of *extruded* polystyrene.

Polystyrene results when styrene monomers interconnect. In the polymerisation, the carbon-carbon π bond of the vinyl group is broken and a new carbon-carbon σ bond is formed, attaching to the carbon of another styrene monomer to the chain.



Polyvinyl Chloride

PVC was accidentally synthesized in 1872 by German chemist Eugen Baumann.. The polymer appeared as a white solid inside a flask of vinyl chloride that had been left exposed to sunlight. **Polyvinyl chloride (PVC)** is the world's third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene. About 40 million tonnes are produced per year. Polyvinyl chloride is one of the world's most widely used polymers. By itself it is quite rigid and used in construction materials such as pipes, house siding, flooring. Addition of plasticizers make it soft and flexible for use in upholstery, electrical insulation, shower curtains and waterproof fabrics. There is some effort being made to phase out this polymer owing to environmental concerns.

Polytetrafluorethylene (PTFE): The Nonstick Coating

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The best-known brand name of PTFE-based formulas is **Teflon** (Figure 10.3.1) Aldehydy Chemours. Chemours is a spin-off of DuPont, which originally discovered the compound in 1938. This highly-crystalline fluorocarbon is exceptionally inert to chemicals and solvents. Water and oils do not wet it, which accounts for its use in cooking ware and other anti-stick applications, including personal care products.

These properties — non-adhesion to other materials, non-wetability, and very low coefficient of friction ("slipperiness") — have their origin in the highly electronegative nature of fluorine whose atoms partly shield the carbon chain. Fluorine's outer electrons are so strongly attracted to its nucleus that they are less available to participate in London (dispersion force) interactions.

Figure 10.3.1 Advertisement of the Happy Pan, a Teflon-coated pan from the 1960s. Source: Wikipedia

Some common addition polymers are listed in Tables 10.3.1 and 10.3.2 Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 10.3.1 Some Addition Polymers.


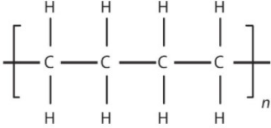
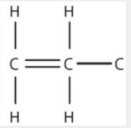
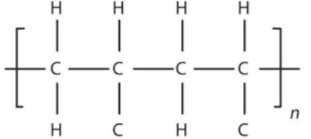
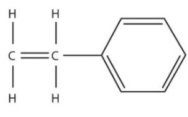
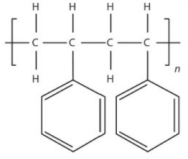
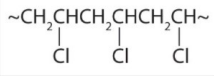
Monomer	Polymer	Polymer Name [Trade Name(s)]	Some Uses
 $\text{CH}_2=\text{CH}_2$	 $\sim\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
 $\text{CH}_2=\text{CHCH}_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
		polystyrene	"take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.
$\text{CH}_2=\text{CHCl}$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$\text{CF}_2=\text{CF}_2$	$\sim\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\sim$	polytetrafluoroethylene (Teflon)	Non-stick coating for cooking utensils, chemically-resistant specialty plastic parts, Gore-Tex

Figure 10.3.2

Table 10.3.2 Other Polymers and their Uses.

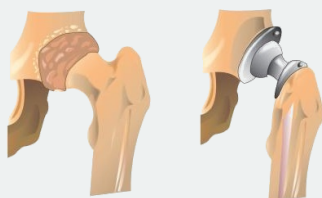
Monomer	Polymer Name	Trade Name(s)	Uses
$\text{H}_2\text{C}=\text{CCl}_2$	polyvinylidene dichloride	Saran	Clinging food wrap
$\text{H}_2\text{C}=\text{CH}(\text{CN})$	polyacrylonitrile	Orlon, Acrilan, Creslan	Fibers for textiles, carpets, upholstery
$\text{H}_2\text{C}=\text{CH}(\text{OCOCH}_3)$	polyvinyl acetate		Elmer's glue - Silly Putty Demo
$\text{H}_2\text{C}=\text{CH}(\text{OH})$	polyvinyl alcohol		Ghostbusters Demo
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$	polymethyl methacrylate	Plexiglass, Lucite	Stiff, clear, plastic sheets, blocks, tubing, and other shapes
$\text{H}_2\text{C}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$	polyisoprene	natural or some synthetic rubber	applications similar to natural rubber
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	polybutadiene	polybutadiene synthetic rubber	select synthetic rubber applications
$\text{H}_2\text{C}=\text{CH}-\text{CCl}=\text{CH}_2$	polychloroprene	Neoprene	chemically-resistant rubber

Processing Polymers

Molding is the process of manufacturing by shaping liquid or pliable raw material using a rigid frame called a mold or matrix. This itself may have been made using a pattern or model of the final object. **Compression molding** is a forming process in which a plastic material is placed directly into a heated metal mold then is softened by the heat and therefore forced to conform to the shape of the mold, as the mold closes. **Transfer molding** (BrE moulding) is a manufacturing process where casting material is forced into a mold. Transfer molding is different from compression molding in that the mold is enclosed [Hayward] rather than open to the fill plunger resulting in higher dimensional tolerances and less environmental impact.

Injection moulding is a manufacturing process for producing parts by injecting molten material into a mould. Injection moulding can be performed with a host of materials mainly including metals (for which the process is called die-casting), glasses, elastomers, confections, and most commonly thermoplastic and thermosetting polymers. **Extrusion** is a process used to create objects of a fixed cross-sectional profile. A material is pushed through a die of the desired cross-section. **Drawing** is a similar process, which uses the tensile strength of the material to pull it through the die. This limits the amount of change which can be performed in one step, so it is limited to simpler shapes, and multiple stages are usually needed. Drawing is the main way to produce wire. Metal bars and tubes are also often drawn.

Medical Uses of Polymers



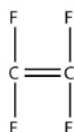
An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

Figure 10.3.2: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Figure

✓ Example 10.3.1

Draw the polymer that results from the polymerization of tetrafluoroethylene.



Solution

In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer that is made has this structure:



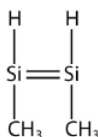
? Exercise 10.3.1

Draw the polymer that results from the polymerization of the following monomers:

a.

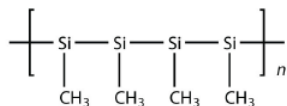


b.



Answers

a.



b.

Summary

- Addition polymerization is when the monomer molecules bond to each other without the loss of any other atoms.
- Examples of addition polymers include polyethylene, polypropylene, polystyrene, polyvinylchloride, polytetrafluoroethylene, etc.
- Many objects in daily use from packing, wrapping, and building materials include half of all polymers synthesized. Other uses include textiles, many electronic appliance casings, CD's, automobile parts, and many others are made from polymers.

Contributors and Attributions

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- Libretext: The Basics of GOB Chemistry (Ball et al.)
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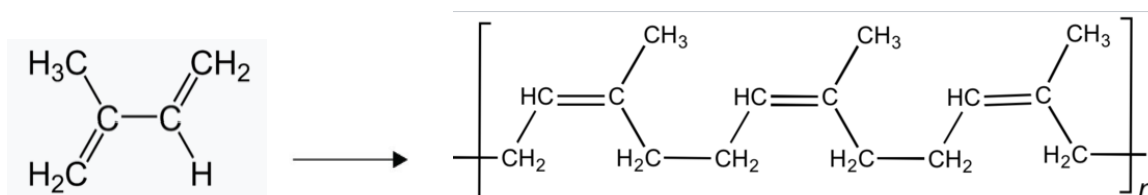
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10.4: Rubber and Other Elastomers

Learning Objectives

- Know the properties of rubber.
- Describe the process of vulcanization.

Natural rubber, also called **India rubber** or **caoutchouc**, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water. Thailand and Indonesia are two of the leading rubber producers. Forms of polyisoprene that are used as natural rubbers are classified as elastomers.



Isoprene Polyisoprene (rubber)

Currently, rubber is harvested mainly in the form of the latex from the rubber tree or others. The latex is a sticky, milky colloid drawn off by making incisions in the bark and collecting the fluid in vessels in a process called "tapping". The latex then is refined into rubber ready for commercial processing. In major areas, latex is allowed to coagulate in the collection cup. The coagulated lumps are collected and processed into dry forms for marketing.

Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience, and is extremely waterproof.

Vulcanization

In 1832–1834 Nathaniel Hayward and Friedrich Ludersdorf discovered that rubber treated with sulfur lost its stickiness. It is likely Hayward shared his discovery with Charles Goodyear, possibly inspiring him to make the discovery of vulcanization. Thomas Hancock (1786–1865), a scientist and engineer, was the first to patent vulcanization of rubber. He was awarded a British patent on May 21, 1845. Three weeks later, on June 15, 1845, Charles Goodyear was awarded a patent in the United States. It was Hancock's friend William Brockedon who coined term 'vulcanization'. Goodyear claimed that he had discovered vulcanization earlier, in 1839.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. Sulfur forms cross-links (bridges) between sections of polymer chain which results in increased rigidity and durability, as well as other changes in the mechanical and electronic properties of the material. A vast array of products are made with vulcanized rubber, including tires, shoe soles, hoses, and conveyor belts. The term *vulcanization* is derived from Vulcan, the Roman god of fire.

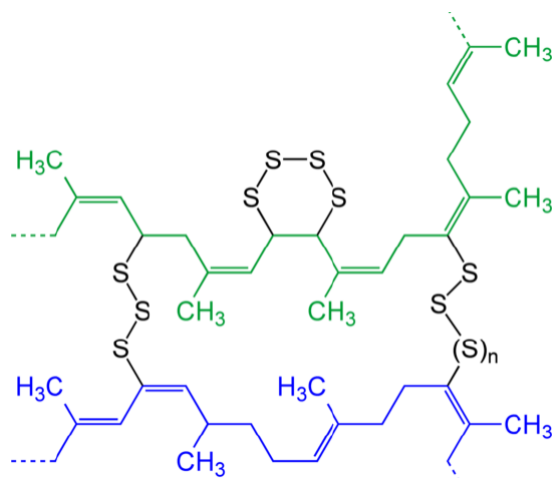


Figure \(\ PageIndex{1}\) General representation of the chemical structure of vulcanized natural rubber showing the crosslinking of two polymer chains (**blue** and **green**) with sulfur ($n = 0, 1, 2, 3 \dots$).

Synthetic Rubber

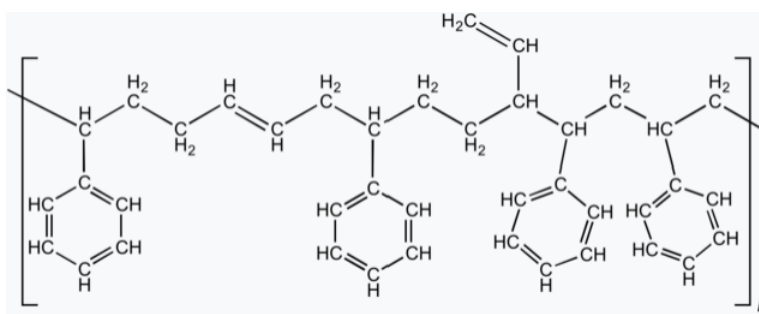
The expanded use of bicycles, and particularly their pneumatic tires, starting in the 1880s, created increased demand for rubber. In 1909 a team headed by Fritz Hofmann, working at the Bayer laboratory in Germany, succeeded in polymerizing isoprene, the first synthetic rubber. A synthetic rubber is any artificial elastomer. These are mainly polymers synthesized from petroleum by products.

Polybutadiene rubber is a polymer formed from the polymerization of the monomer 1,3-butadiene. Polybutadiene has a high resistance to wear and is used especially in the manufacture of tires, which consumes about 70% of the production. Another 25% is used as an additive to improve the toughness (impact resistance) of plastics such as polystyrene and acrylonitrile butadiene styrene (ABS). Polybutadiene rubber accounted for about a quarter of total global consumption of synthetic rubbers in 2012. It is also used to manufacture golf balls, various elastic objects and to coat or encapsulate electronic assemblies, offering high electrical resistivity.

Neoprene (also **polychloroprene** or **pc-rubber**) is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene exhibits good chemical stability and maintains flexibility over a wide temperature range. Neoprene is sold either as solid rubber or in latex form and is used in a wide variety of applications, such as laptop sleeves, orthopaedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts. Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.

Free radical production of neoprene.png

Styrene-butadiene or **styrene-butadiene rubber (SBR)** describe families of synthetic rubbers derived from styrene and butadiene (the version developed by Goodyear is called **Neolite**). These materials have good abrasion resistance and good aging stability when protected by additives. In 2012, more than 5.4 million tonnes of SBR were processed worldwide. About 50% of car tires are made from various types of SBR.



It is a commodity material which competes with natural rubber. The elastomer is used widely in pneumatic tires. Other uses include shoe heels and soles, gaskets, and even chewing gum.

Polymers in Paints

Polymers are one of the key components of modern paints that function as binders. The binder is the film-forming component of paint. It is the only component that is always present among all the various types of formulations. The binder imparts properties such as gloss, durability, flexibility, and toughness. Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, or siloxanes or oils.

Summary

The many uses of natural rubber has led to development and manufacture of synthetic rubber.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators.

Three examples of synthetic rubber used in various applications are polybutadiene, polychloroprene (Neoprene), and styrene-butadiene rubber (SBR)

Contributors and Attributions

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10.5: Condensation Polymers

Learning Objectives

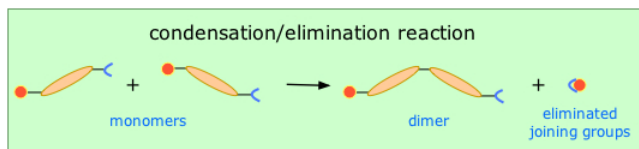
- Know the difference between addition and condensation polymerization.
- Know the properties and uses of common synthetic condensation polymers.

A large number of important and useful polymeric materials are not formed by addition polymerization, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as step-growth polymers. In contrast to addition polymerization, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

Examples of naturally occurring condensation polymers are cellulose, starch, the polypeptide chains of proteins, and poly(β -hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria.

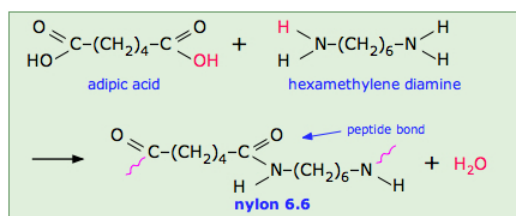
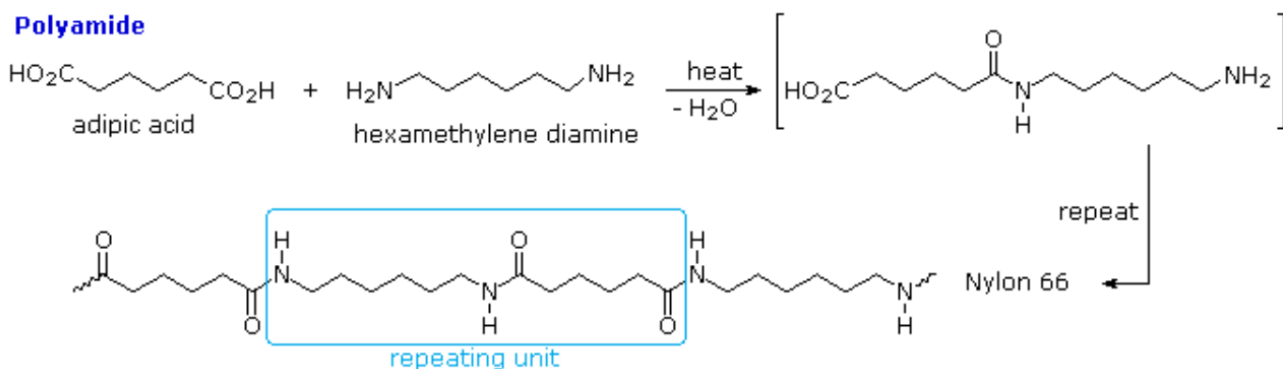
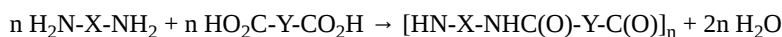
Nylon and Other Polyamides

Condensation polymerization (also known as *step-growth*) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H_2O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together.



One important class of condensation polymers are polyamides. They arise from the reaction of carboxylic acid and an amine. Examples include nylons and proteins.

When prepared from diamines and dicarboxylic acids, e.g. the production of nylon 66, the polymerization produces two molecules of water per repeat unit:



Note that the monomeric units that make up the polymer are not identical with the starting components.

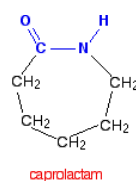
Nylon is a thermoplastic silky material that can be melt-processed into fibers, films, or shapes.^{:2} It is made of repeating units linked by amide links similar to the peptide bonds in proteins. Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations. Nylon polymers have found significant commercial applications in fabric and fibers (apparel, flooring and rubber reinforcement), in shapes (molded parts for cars, electrical equipment, etc.), and in films (mostly for food packaging).

Figure 10.5.1 Wallace H. Carothers

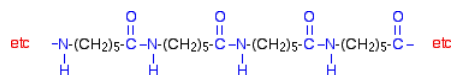
Nylon was the first commercially successful synthetic thermoplastic polymer. DuPont began its research project in 1927. The first example of nylon (nylon 6,6) was produced using diamines on February 28, 1935, by Wallace Hume Carothers (Figure 10.5.1) at DuPont's research facility at the DuPont Experimental Station. In response to Carothers' work, Paul Schlack at IG Farben developed nylon 6, a different molecule based on caprolactam, on January 29, 1938.^{:10}

Nylon was first used commercially in a nylon-bristled toothbrush in 1938, followed more famously in women's stockings or "nylons" which were shown at the 1939 New York World's Fair and first sold commercially in 1940. During World War II, almost all nylon production was diverted to the military for use in parachutes and parachute cord. Wartime uses of nylon and other plastics greatly increased the market for the new materials.

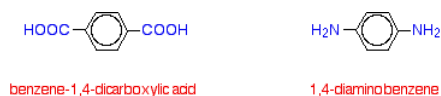
Other polyamides of practical use include nylon 6 and kevlar. Nylon-6 is made from a monomer called caprolactam.



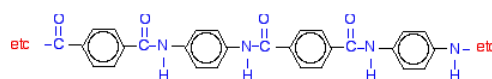
Notice that this already contains an amide link. When this molecule polymerizes, the ring opens, and the molecules join up in a continuous chain. Nylon 6 fibers are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkleproof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb up to 2.4% of water, although this lowers tensile strength.



Kevlar is similar in structure to nylon-6,6 except that instead of the amide links joining chains of carbon atoms together, they join benzene rings. The two monomers are benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene.



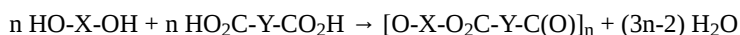
If you line these up and remove water between the -COOH and -NH₂ groups in the same way as we did with nylon-6,6, you get the structure of Kevlar:



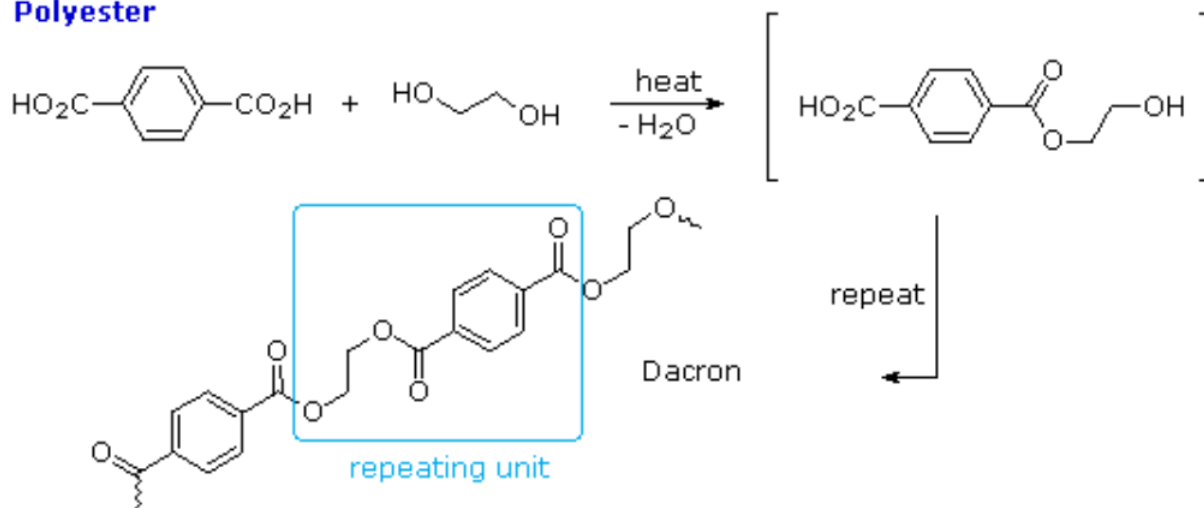
Kevlar is a very strong material - about five times as strong as steel, weight for weight. It is used in bulletproof vests, in composites for boat construction, in lightweight mountaineering ropes, and for lightweight skis and racquets - amongst many other things.

Polyethylene Terephthalate and Other Polyesters

One important class of condensation polymers are polyesters. They arise from the reaction of carboxylic acid and an alcohol. Examples include polyesters, e.g. polyethyleneterephthalate:



Polyester



Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated **PET**, **PETE**, or the obsolete PETP or PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins.

It may also be referred to by the brand names **Terylene** in the UK, **Lavsan** in Russia and the former Soviet Union, and **Dacron** in the US.

The majority of the world's PET production is for synthetic fibres (in excess of 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred to by its common name, polyester, whereas the acronym *PET* is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC).

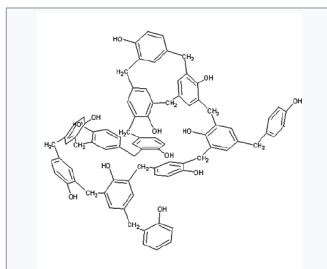
Phenol-Formaldehyde and Related Resins

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical nonconductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.

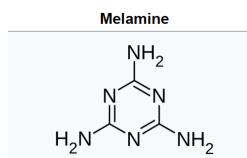
In recent years the "retro" appeal of old Bakelite products has made them collectible.

Bakelite was designated a National Historic Chemical Landmark on November 9, 1993, by the American Chemical Society in recognition of its significance as the world's first synthetic plastic.

Bakelite



Melamine ⁱ/mɛləˈmiːn/ (About this sound)listen) is an organic compound with the formula $C_3H_6N_6$. This white solid is a trimer of cyanamide, with a 1,3,5-triazine skeleton. Like cyanamide, it contains 67% nitrogen by mass, and its derivatives have fire retardant properties due to its release of nitrogen gas when burned or charred. Melamine can be combined with formaldehyde and other agents to produce melamine resins. Such resins are characteristically durable thermosetting plastic used in high pressure decorative laminates such as Formica, melamine dinnerware, laminate flooring, and dry erase boards. Melamine foam is used as insulation, soundproofing material and in polymeric cleaning products, such as Magic Eraser.



Other Condensation Polymers

Polycarbonates (PC) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. Polycarbonates received their name because they are polymers containing carbonate groups ($-\text{O}-(\text{C}=\text{O})-\text{O}-$). A balance of useful features, including temperature resistance, impact resistance and optical properties, positions polycarbonates between commodity plastics and engineering plastics.

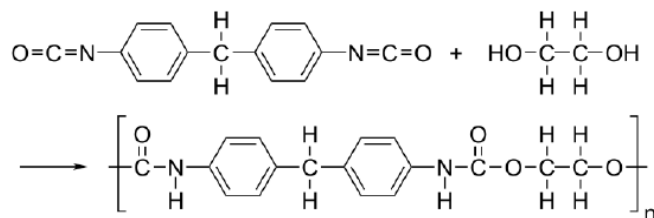
The main polycarbonate material is produced by the reaction of bisphenol A (BPA) and phosgene COCl_2 . The overall reaction can be written as follows:



Polycarbonate is mainly used for electronic applications that capitalize on its collective safety features. Being a good electrical insulator and having heat-resistant and flame-retardant properties. The second largest consumer of polycarbonates is the construction industry, e.g. for domelights, flat or curved glazing, and sound walls, which all use extruded flat solid or multiwall sheet, or corrugated sheet. A major application of polycarbonate is the production of Compact Discs, DVDs, and Blu-ray Discs.

Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.

Polyurethanes are in the class of compounds called **reaction polymers**, which include epoxies, unsaturated polyesters, and phenolics. Polyurethanes are produced by reacting an isocyanate containing two or more isocyanate groups per molecule ($\text{R}-(\text{N}=\text{C}=\text{O})_n$) with a polyol containing on average two or more hydroxyl groups per molecule ($\text{R}'-(\text{OH})_n$) in the presence of a catalyst or by activation with ultraviolet light.



Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms, and hoses.

Figure 10.5.2 A polyurethane foam sponge.

Health and Safety

Fully reacted polyurethane polymer is chemically **inert**. No exposure limits have been established in the U.S. by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity.

Figure 10.5.3 *Open-flame test. Top, untreated polyurethane foam burns vigorously. Bottom, with fire-retardant treatment.*

Polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame. Decomposition from fire can produce significant amounts of carbon monoxide and hydrogen cyanide, in addition to nitrogen oxides, isocyanates, and other toxic products. Because of the flammability of the material, it has to be treated with flame retardants (at least in case of furniture), almost all of which are considered harmful. California later issued Technical Bulletin 117 2013 which allowed most

polyurethane foam to pass flammability tests without the use of flame retardants. Green Science Policy Institute states: "Although the new standard can be met without flame retardants, it does NOT ban their use. Consumers who wish to reduce household exposure to flame retardants can look for a TB117-2013 tag on furniture, and verify with retailers that products do not contain flame retardants."

Liquid resin blends and isocyanates may contain hazardous or regulated components. Isocyanates are known skin and respiratory sensitizers. Additionally, amines, glycols, and phosphate present in spray polyurethane foams present risks.

Exposure to chemicals that may be emitted during or after application of polyurethane spray foam (such as isocyanates) are harmful to human health and therefore special precautions are required during and after this process.

In the United States, additional health and safety information can be found through organizations such as the Polyurethane Manufacturers Association (PMA) and the Center for the Polyurethanes Industry (CPI), as well as from polyurethane system and raw material manufacturers. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment). In Europe, health and safety information is available from ISOPA, the European Diisocyanate and Polyol Producers Association.

Epoxy is either any of the basic components or the cured end products of **epoxy resins**, as well as a colloquial name for the epoxide functional group. Epoxy resins, also known as **polyepoxides**, are a class of reactive prepolymers and polymers which contain epoxide groups.

Epoxy resins may be reacted (cross-linked) either with themselves through catalytic homopolymerisation, or with a wide range of co-reactants including polyfunctional amines, acids (and acid anhydrides), phenols, alcohols and thiols (usually called mercaptans). These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing. The structure of bisphenol-A diglycidyl ether epoxy resin is shown below: n denotes the number of polymerized subunits and is typically in the range from 0 to 25



Figure 10.5.4 Bisphenol-A diglycidyl ether epoxy.

Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with favorable mechanical properties and high thermal and chemical resistance. Epoxy has a wide range of applications, including metal coatings, use in electronics/electrical components/LEDs, high tension electrical insulators, paint brush manufacturing, fiber-reinforced plastic materials and structural adhesives. Epoxy is sometimes used as a glue (see image at right).

Figure 10.5.5 A 5-minute epoxy glue.

Composite Materials

A **composite material** (also called a **composition material** or shortened to **composite**, which is the common name) is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.

Composites are made up of individual materials referred to as constituent materials. There are two main categories of constituent materials: **matrix** (binder) and **reinforcement**. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Many commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK (polyether ether ketone), and others. Common fibres used for reinforcement include glass fibres, carbon fibres, cellulose (wood/paper fibre and straw) and high strength polymers for example aramid. Silicon carbide fibers are used for some high temperature applications.

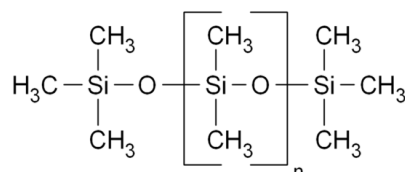
One of the most common and familiar composite is fiberglass, in which small glass fibre are embedded within a polymeric material (normally an epoxy or polyester). The glass e is relatively strong and stiff (but also brittle), whereas the polymer is ductile (but also

weak and flexible). Thus the resulting fibreglass is relatively stiff, strong, flexible, and ductile.

Figure 10.5.6 Glass reinforcements used for fiberglass are supplied in different physical forms, microspheres, chopped or woven.

Silicones

Silicones, also known as **polysiloxanes**, are polymers that include any synthetic compound made up of repeating units of siloxane. Silicones consist of an inorganic silicon-oxygen backbone chain ($\cdots\text{Si-O-Si-O-Si-O}\cdots$) with organic side groups attached to the silicon atoms. Silicones have in general the chemical formula $[\text{R}_2\text{SiO}]_n$, where R is an organic group such as an alkyl (methyl, ethyl) or phenyl group. A silicone polymer that consists of repeated units of dimethyl silicone is shown below.



They are typically heat-resistant and either liquid or rubber-like. Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants and cooking utensils), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine and dentistry (e.g., tooth impression molds), textiles and paper (e.g., coatings). For these applications, an estimated 400,000 tonnes of silicones were produced in 1991.

Figure 10.5.7 Soup ladle and pasta ladle made of silicone.

📌 Silicone vs Silicon

Silicone is often confused with silicon, but they are distinct substances. Silicon is a chemical element, a hard dark-grey semiconducting metalloid which in its crystalline form is used to make integrated circuits ("electronic chips") and solar cells. Silicones are compounds that contain silicon, carbon, hydrogen, oxygen, and perhaps other kinds of atoms as well, and have very different physical and chemical properties.

Summary

- Condensation polymerization (also known as *step-growth*) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H_2O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together.
- Examples of natural condensation polymers include cellulose, starch, and polypeptide chains of proteins.
- Several synthetic condensation polymers discussed include nylon, kevlar, polyester, Bakelite, Melamine, polycarbonates, polyurethanes, epoxies.
- Synthetic condensation polymers have a wide array of household, industrial, commercial, and medical uses and applications.

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10.6: Properties of Polymers

Learning Objectives

- Know the properties of polymers based on their molecular and intermolecular structures.
- Know the relationship between degree of crystallinity to physical properties of polymers.

The physical properties of a polymer such as its strength and flexibility depend on:

- *chain length* - in general, the longer the chains the stronger the polymer;
- *side groups* - polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- *branching* - straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- *cross-linking* - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

Crystalline and Amorphous Polymers

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. For many polymers, reduced crystallinity may also be associated with increased transparency.

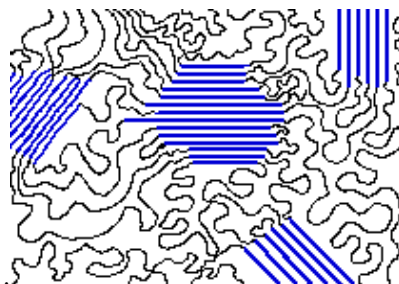


Figure 10.6.1 The crystalline parts of this polymer are shown in blue.

Depending on the degree of crystallinity, there will be a higher temperature, the *melting point* t_m , at which the crystalline regions come apart and the material becomes a viscous liquid. Such liquids can easily be injected into molds to manufacture objects of various shapes, or extruded into sheets or fibers. Other polymers (generally those that are highly cross-linked) do not melt at all; these are known as *thermosets*. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially-produced polymers are thermosets; the remainder are thermoplastics.

The Glass Transition Temperature

In some polymers (known as *thermoplastics*) there is a fairly definite softening point that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbors, thus rendering them more flexible and deformable. This defines the *glass transition temperature* t_g . Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, i.e., when they are in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g , that is, in the rubbery state, where they are soft and flexible.

Fiber Formation

Bill Pittendreich, DuPont, and other individuals and corporations worked diligently during the first few months of World War II to find a way to replace Asian silk and hemp with nylon in parachutes. It was also used to make tires, tents, ropes, ponchos, and other military supplies. It was even used in the production of a high-grade paper for U.S. currency. At the outset of the war, cotton accounted for more than 80% of all fibers used and manufactured, and wool fibers accounted for nearly all of the rest. By August 1945, manufactured fibers had taken a market share of 25%, at the expense of n. After the war, e of shortages of both silk and nylon, nylon parachute material was sometimes repurposed to make dresses. Nylon 6 and 66 fibers are used in carpet manufacture. Nylon is one kind of fibers used in tire cord. Herman E. Schroeder pioneered application of nylon in tires.

Figure 10.6.2 Blue nylon fabric ball gown by Emma Domb, Science History Institute.

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered ure and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact, the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

Figure 10.6.3 Stretching polyester fabric.

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of -100,000, about 1900 monomer units. For a fiber to be called "acrylic" in the US, the polymer must contain at least 85% acrylonitrile monomer. Typical comonomers are vinyl acetate or methyl acrylate. DuPont created the first acrylic fibers in 1941 and trademarked them under the name **Orlon**. It was first developed in the mid-1940s but was not produced in large quantities until the 1950s. Strong and warm, acrylic fiber is often used for sweaters and tracksuits and as linings for boots and gloves, as well as in furnishing fabrics and carpets. It is manufactured as a filament, then cut into short staple lengths similar to wool hairs, and spun into yarn.

Modacrylic is a modified acrylic fiber that contains at least 35% and at most 85% acrylonitrile monomer. The comonomers vinyl chloride, vinylidene chloride or vinyl bromide used in modacrylic give the fiber flame retardant properties. End-uses of modacrylic include faux fur, wigs, hair extensions and protective clothing.

Microfiber (or **microfibre**) is synthetic fiber finer than one denier or decitex/thread, having a diameter of less than ten micrometres. This is smaller than the diameter of a strand of silk (which is approximately one denier), which is itself about 1/5 the diameter of a human hair.



Figure 10.6.4 Close-up view of microfiber (left) and microfiber household cloth (right).

The most common types of microfibers are made from polyesters, polyamides (e.g., nylon, Kevlar, Nomex, tregamide), or a conjugation of polyester, polyamide, and polypropylene. Microfiber is used to make mats, knits, and weaves for apparel, upholstery, industrial filters, and cleaning products. The shape, size, and combinations of synthetic fibers are selected for specific characteristics, including softness, toughness, absorption, water repellency, electrostatics, and filtering capabilities.

Environmental and Safety Issues

Microfiber textiles tend to be flammable if manufactured from hydrocarbons (polyester) or carbohydrates (cellulose) and emit toxic gases when burning, more so if aromatic (PET, PS, ABS) or treated with halogenated flame retardants and azo dyes. Their polyester and nylon stock are made from petrochemicals, which are not a renewable resource and are not biodegradable. However, if made out of polypropylene, they are recyclable (Prolen).

For most cleaning applications they are designed for repeated use rather than being discarded after use. An exception to this is the precise cleaning of optical components where a wet cloth is drawn once across the object and must not be used again as the debris collected are now embedded in the cloth and may scratch the optical surface.

Microfiber that is made from petrochemicals includes polyester and nylon which are not biodegradable. However, microfiber made from polypropylene can be recyclable. Microfiber products may also have the potential of entering the oceanic water supply and food chain similar to other microplastics. Synthetic clothing made of microfibers that are washed can release materials and travel to local wastewater treatment plants, contributing to plastic pollution in water. Fibers retained in wastewater treatment sludge (biosolids) that are land-applied can persist in soils.

There are environmental concerns about this product entering the oceanic food chain similar to other microplastics. A study by the clothing brand Patagonia and University of California, Santa Barbara, found that when synthetic jackets made of microfibers are washed, on average 1.7 grams (0.060 oz) of microfibers are released from the washing machine. These microfibers then travel to local wastewater treatment plants, where up to 40% of them enter into rivers, lakes, and oceans where they contribute to the overall plastic pollution. Microfibers account for 85% of man-made debris found on shorelines worldwide.

However, no pesticides are used for producing synthetic fibers (in comparison to cotton). If these products are made of polypropylene yarn, the yarn is dope-dyed; i.e. no water is used for dyeing (as with cotton, where thousands of liters of water become contaminated).

Summary

- The physical properties of a polymer such as its strength and flexibility depend on chain length, side groups present, branching, and cross-linking.
- Synthetic polymers may consist of both crystalline (more ordered, crystal-like) and amorphous (less ordered) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.
- The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.
- Due to their chemical structure, nylon, polyester, and acrylic fibers have physical properties that are comparable or even superior to natural fibers. Thus, many of these fibers have a variety of uses and have replaced natural fibers in various products.

Contributors and Attributions

- Stephen Lower, Professor Emeritus ([Simon Fraser U.](#)) [Chem1 Virtual Textbook](#) IF Figure is used
- [Marisa Alviar-Agnew](#) ([Sacramento City College](#))
- Wikipedia

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10.7: Plastics and the Environment

Learning Objectives

- Know the problems associated with plastics.
- Identify the type of polymer associated with each recycling number.
- Know the different plastic recycling processes.

Problems with Plastics

Due to their low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in a multitude of products of different scale, including paper clips and spacecraft. They have prevailed over traditional materials, such as wood, stone, horn and bone, leather, metal, glass, and ceramic, in some products previously left to natural materials. However, there are numerous problems encountered with plastic use.

Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, uv absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic — and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

Perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

Decomposition products

Most commonly-used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. And what decomposition does occur will combine with rainwater to form *leachates* that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard. Disposed products containing **fluorocarbons** (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

Hazards to animals

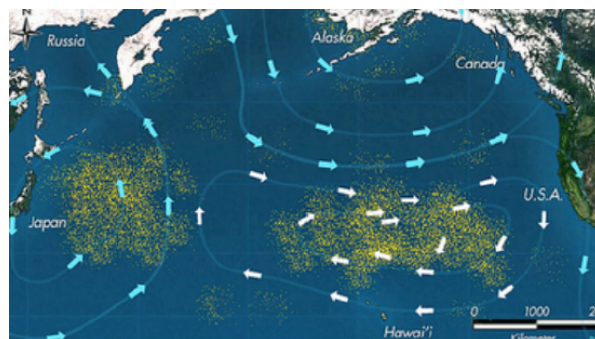
There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in (Figure 10.7.1).



Figure 10.7.1 A plastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and a slow death (left) remains of an albatross that mistook bits of plastic junk for food (right).

These dangers occur throughout the ocean, but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres that have accumulated astounding quantities of plastic waste.



Recycling

The huge quantity (one estimate is 10^8 metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste which is difficult to incinerate safely and which, being largely non-biodegradable, threatens to overwhelm the capacity of landfills. An additional consideration is that *de novo* production most of the major polymers consumes non-renewable hydrocarbon resources.



Figure 10.7.2 Plastic water bottles present a special recycling problem because of their widespread use in away-from-home locations.

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle (they practically disappeared during the recession that commenced in 2008.)
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types necessitates their separation into different waste streams — usually requiring manual (i.e., low-cost) labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the availability of recycled materials in the countries in which the plastics originated.

Some of the major recycling processes include

- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem.
- A very small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- Thermopolymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatibility problems.
- Thermosets are usually shredded and used as filler material in recycled thermopolymers.

Other processes

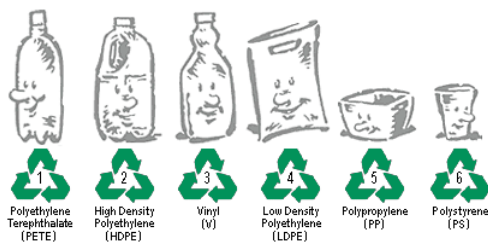
A process has also been developed in which many kinds of plastic can be used as a carbon source in the recycling of scrap steel. There is also a possibility of mixed recycling of different plastics, which does not require their separation. It is called compatibilization and requires use of special chemical bridging agents compatibilizers. It can help to keep the quality of recycled material and to skip often expensive and inefficient preliminary scanning of waste plastics streams and their separation/purification.

Figure 10.7.3 *Plastic or other polymer compatibilization.*

Recycled Plastics

Seven groups of plastic polymers, each with specific properties, are used worldwide for packaging applications (see Table 10.7.1). Each group of plastic polymer can be identified by its plastic identification code (PIC), usually a number or a letter abbreviation. For instance, low-density polyethylene can be identified by the number "4" or the letters "LDPE". The PIC appears inside a three-chasing-arrow recycling symbol. The symbol is used to indicate whether the plastic can be recycled into new products.

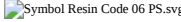

The PIC was introduced by the Society of the Plastics Industry, Inc., to provide a uniform system for the identification of various polymer types and to help recycling companies separate various plastics for reprocessing. Manufacturers of plastic products are required to use PIC labels in some countries/regions and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food/chemical packaging and containers.



Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.

Table 10.7.1 The Major Groups of Plastic Polymers. Source: Wikipedia

Plastic identification code	Type of plastic polymer	Properties	Common packaging applications	Melting temperatures (°C)
	Polyethylene terephthalate(PET, PETE)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars; ice cream cone lids; small consumer electronics	T _m = 250
	High-density polyethylene(HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas	Water pipes, Gas & Fire Pipelines , Electrical & Communications conduit, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles	T _m = 130
	Polyvinyl chloride(PVC)	Versatility, ease of blending, strength, toughness.	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.	T _m = 240
	Low-density polyethylene(LDPE)	Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture	Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids	T _m = 120
	Polypropylene(PP)	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.	T _m = 173

	Polystyrene(PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers	T _m = 240
	Other (often polycarbonate or ABS)	Dependent on polymers or combination of polymers	Beverage bottles, baby milk bottles. Non-packaging uses for polycarbonate, compact discs, "unbreakable" glazing, electronic apparatus housing, lenses (including sunglasses), prescription glasses, automotive headlamps, riot shields, instrument panels.	Polycarbonate: T _m = 225

Tire Recycling

The large number of rubber tires that are disposed of, together with the increasing reluctance of landfills to accept them, has stimulated considerable innovation in the re-use of this material, especially in the construction industry.

Plastics and Fire Hazards

The term *fire (or flame)-retardant* as applied to organic (i.e., containing carbon) materials, is intended to refer to *reduced* fire hazard, as all will burn under certain circumstances. Fabric flammability is an important textile issue, especially for stage drapery that will be used in a public space such as a school, theatre or special event venue. In the United States, Federal regulations require that drapery fabrics used in such spaces be certified as flame or fire-retardant. For draperies and other fabrics used in public places, this is known as the NFPA 701 Test, which follows standards developed by the National Fire Protection Association (NFPA). Although all fabrics will burn, some are naturally more resistant to fire than others. Those that are more flammable can have their fire resistance drastically improved by treatment with fire-retardant chemicals. Inherently flame-retardant fabrics such as polyester are commonly used for flame retardant curtain fabrics.

The deaths in fiery crashes of race car drivers Fireball Roberts at Charlotte, and Eddie Sachs and Dave MacDonald at Indianapolis in 1964 led to the use of flame-resistant ics such as Nomex. Nomex and related aramid polymers are related to nylon, but have aromatic backbones, and hence are more rigid and more durable. Nomex is an example of a *meta* variant of the aramids (Kevlar is a *para* aramid). Unlike Kevlar, Nomex strands cannot align during filament polymerization and has less strength. However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

A Nomex hood is a common piece of racing and firefighting equipment. It is placed on the head on top of a firefighter's face mask. The hood protects the portions of the head not covered by the helmet and face mask from the intense heat of the fire.

Figure 10.7.4 A firefighter in Toronto, Canada wears a Nomex hood in 2007.

Wildland firefighters wear Nomex shirts and trousers as part of their personal protective equipment during wildfire suppression activities.

Racing car drivers wear driving suits constructed of Nomex and or other fire retardant materials, along with Nomex gloves, long underwear, balaclavas, socks, helmet lining and shoes, to protect them in the event of a fire.

Military pilots and aircrew wear flight suits made of over 92 percent Nomex to protect them from the possibility of cockpit fires and other mishaps. Recently, troops riding in ground vehicles have also begun wearing Nomex. Kevlar thread is often used to hold the fabric together at seams.

Military tank drivers also typically use Nomex hoods as protection against fire.

Plasticizers and Pollution

Plasticizers (UK: **plasticisers**) or **dispersants** are additives that increase the plasticity or decrease the viscosity of a material. These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition

temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other. Many (but not all) are small enough to be diffusible and a potential source of health problems.

Polyvinyl chloride polymers are one of the most widely-plasticized types, and the odors often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment.

The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim.

According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe.

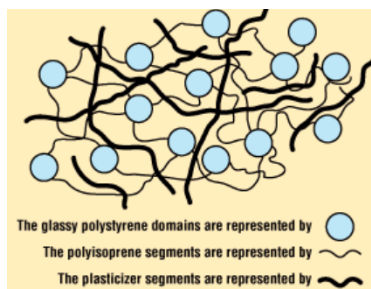


Figure 10.7.5 Shares of global plasticizer consumption in 2014 (8 million metric tons).

Substantial concerns have been expressed over the safety of some plasticizers, especially because some low molecular weight ortho-phthalates have been classified as potential endocrine disruptors with some developmental toxicity reported.

Summary

- Plastics are found everywhere due to its low cost, versatility, ease of use etc.
- Plastics pose a threat to the environment due to residual or degradation products that contribute to air and water pollution.
- Plastics hazards to animals and marine life as these living creatures mistake them for food.
- Plastic polymers are classified into seven groups for recycling purposes.

Contributors and Attributions

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