Fiber Materials and Technology

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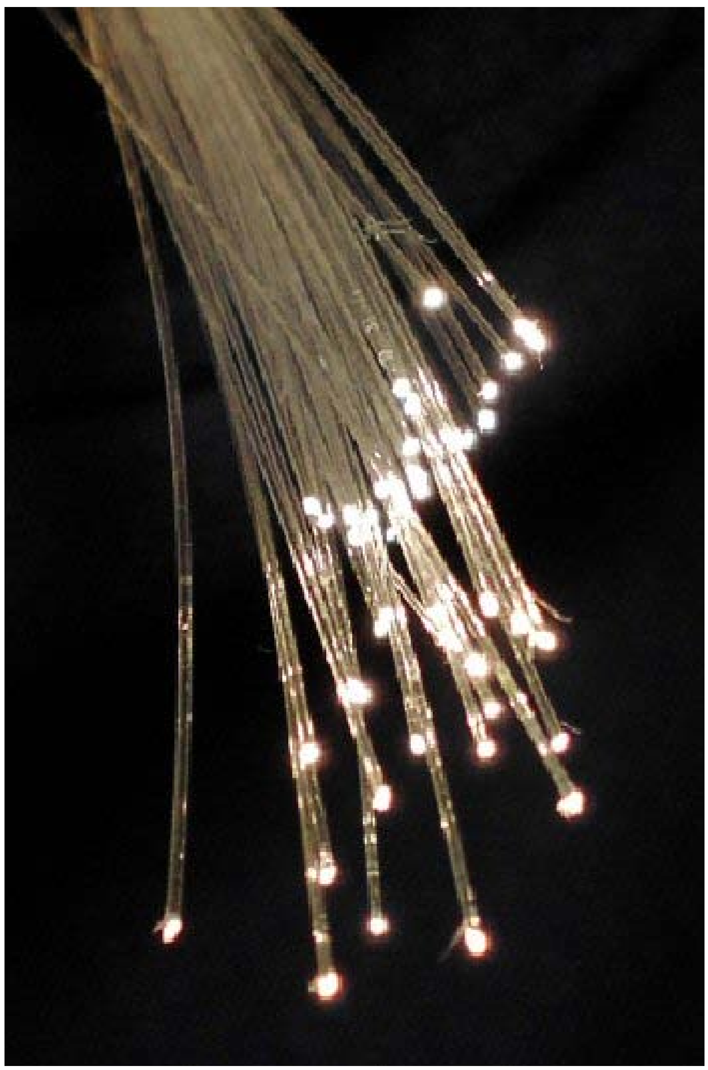
Fiber



A bundle of optical fibers

Fiber, also spelled **fibre**, is a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread.

They are very important in the biology of both plants and animals, for holding tissues together.

Human uses for fibers are diverse. They can be spun into filaments, string or rope, used as a component of composite materials, or matted into sheets to make products such as paper or felt. Fibers are often used in the manufacture of other materials. The strongest engineering materials are generally made as fibers, for example carbon fiber and Ultra-high-molecular-weight polyethylene.

Synthetic fibers can often be produced very cheaply and in large amounts compared to natural fibers, but for clothing natural fibers can give some benefits, such as comfort, over their man-made counterparts.

Textile fiber

A unit in which many complicated textile structures are built up is said to be textile fiber.

Natural fibers

Natural fibers include those produced by plants, animals, and geological processes. They are biodegradable over time. They can be classified according to their origin:

- Vegetable fibers are generally based on arrangements of cellulose, often with lignin: examples include cotton, hemp, jute, flax, ramie, and sisal. Plant fibers are employed in the manufacture of paper and textile (cloth), and dietary fiber is an important component of human nutrition.
- Wood fiber, distinguished from vegetable fiber, is from tree sources. Forms include groundwood, thermomechanical pulp (TMP) and bleached or unbleached kraft or sulfite pulps. Kraft and sulfite, also called sulphite, refer to the type of pulping process used to remove the lignin bonding the original wood structure, thus freeing the fibers for use in paper and engineered wood products such as fiberboard.
- Animal fibers consist largely of particular proteins. Instances are spider silk, sinew, catgut, wool and hair such as cashmere, mohair and angora, fur such as sheepskin, rabbit, mink, fox, beaver, etc.
- Mineral fibers comprise asbestos. Asbestos is the only naturally occurring long mineral fiber. Short, fiber-like minerals include wollastonite, attapulgite and halloysite.

Man-made fibers

Synthetic or **man-made fibers** generally come from synthetic materials such as petrochemicals. But some types of synthetic fibers are manufactured from natural cellulose, including rayon, modal, and the more recently developed Lyocell. Cellulose-based fibers are of two types, regenerated or pure cellulose such as from the cupro-ammonium process and modified cellulose such as the cellulose acetates.

Fiber classification in reinforced plastics falls into two classes: (i) short fibers, also known as discontinuous fibers, with a general aspect ratio (defined as the ratio of fiber length to diameter) between 20 to 60, and (ii) long fibers, also known as continuous fibers, the general aspect ratio is between 200 to 500.

Cellulose fibers

- Cellulose fibers are a subset of man-made fibers, regenerated from natural cellulose. The cellulose comes from various sources. Modal is made from beech trees, bamboo fiber is a cellulose fiber made from bamboo, seacell is made from seaweed, etc.

Mineral fibers

Mineral fibers can be particular strong because they are formed with a low number of surface defects.

- Fiberglass, made from specific glass, and optical fiber, made from purified natural quartz, are also man-made fibers that come from natural raw materials, silica fiber, made from sodium silicate (water glass) and basalt fiber made from melted basalt.
- Metallic fibers can be drawn from ductile metals such as copper, gold or silver and extruded or deposited from more brittle ones, such as nickel, aluminum or iron.
- Carbon fibers are often based on oxydized and carbonised polymers, but the end product is almost pure carbon.

Polymer fibers

- Polymer fibers are a subset of man-made fibers, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process. These fibers are made from:
    - polyamide nylon,
    - PET or PBT polyester
    - phenol-formaldehyde (PF)
    - polyvinyl alcohol fiber (PVA)
    - polyvinyl chloride fiber (PVC)
    - polyolefins (PP and PE)
    - acrylic polyesters, pure polyester PAN fibers are used to make carbon fiber by roasting them in a low oxygen environment. Traditional acrylic fiber is used more often as a synthetic replacement for wool. Carbon fibers

and PF fibers are noted as two resin-based fibers that are not thermoplastic, most others can be melted.
- Aromatic polyamids (aramids) such as Twaron, Kevlar and Nomex thermally degrade at high temperatures and do not melt. These fibers have strong bonding between polymer chains
- polyethylene (PE), eventually with extremely long chains / HMPE (e.g. Dyneema or Spectra).
- Elastomers can even be used, e.g. spandex although urethane fibers are starting to replace spandex technology.
- polyurethane fiber

- Coextruded fibers have two distinct polymers forming the fiber, usually as a core-sheath or side-by-side. Coated fibers exist such as nickel-coated to provide static elimination, silver-coated to provide anti-bacterial properties and aluminum-coated to provide RF deflection for radar chaff. Radar chaff is actually a spool of continuous glass tow that has been aluminum coated. An aircraft-mounted high speed cutter chops it up as it spews from a moving aircraft to confuse radar signals.

Microfibers

Microfibers in textiles refer to sub-denier fiber (such as polyester drawn to 0.5 dn). Denier and Detex are two measurements of fiber yield based on weight and length. If the fiber density is known you also have a fiber diameter, otherwise it is simpler to measure diameters in micrometers. Microfibers in technical fibers refer to ultra fine fibers (glass or meltblown thermoplastics) often used in filtration. Newer fiber designs include extruding fiber that splits into multiple finer fibers. Most synthetic fibers are round in cross-section, but special designs can be hollow, oval, star-shaped or trilobal. The latter design provides more optically reflective properties. Synthetic textile fibers are often crimped to provide bulk in a woven, non woven or knitted structure. Fiber surfaces can also be dull or bright. Dull surfaces reflect more light while bright tends to transmit light and make the fiber more transparent.

Very short and/or irregular fibers have been called fibrils. Natural cellulose, such as cotton or bleached kraft, show smaller fibrils jutting out and away from the main fiber structure.

Chapter- 2

Natural Fiber and Synthetic Fiber

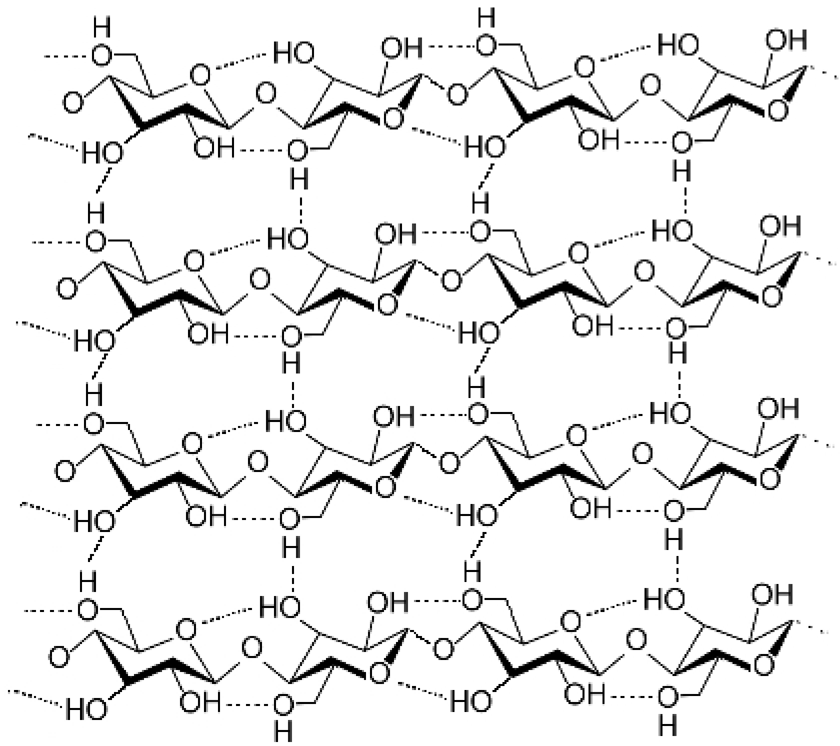
Natural fiber

Fibers or **fibres** are a class of hair-like materials that are continuous filaments or are in discrete elongated pieces, similar to pieces of thread. They can be spun into filaments, thread, or rope. They can be used as a component of composite materials. They can also be matted into sheets to make products such as paper or felt. Fibers are of three types: natural fiber, cellulose fiber, and synthetic fiber. The earliest evidence for humans using fibers is the discovery of wool and dyed flax fibers found in a prehistoric cave in the Republic of Georgia that date back to 36,000 BP.

Sources

Natural fibers are made from plant, animal and mineral sources. Natural fibers can be classified according to their origin.

Vegetable fibers



A strand of cellulose (conformation I_{α}), showing the hydrogen bonds (dashes) within and between cellulose molecules

Vegetable fibers are generally composed mainly of cellulose: examples include cotton, jute, flax, ramie, sisal, and hemp. Cellulose fibers serve in the manufacture of paper and cloth. This fiber can be further categorized into the following:

Category	Description
Seed fiber	Fibers collected from seeds or seed cases. e.g. cotton and kapok
Leaf fiber	Fibers collected from leaves. e.g. fique, sisal, banana and agave.
Bast fiber skin fiber	Fibers are collected from the skin or bast surrounding the stem of their respective plant. These fibers have higher tensile strength than other fibers. Therefore, these fibers are used for durable yarn, fabric, packaging, and paper. Some examples are flax, jute, kenaf, industrial hemp, ramie, rattan, and vine fibers.
Fruit fiber	Fibers are collected from the fruit of the plant, e.g. coconut (coir) fiber.
Stalk fiber	Fibers are actually the stalks of the plant. E.g. straws of wheat, rice, barley, and other crops including bamboo and grass. Tree wood is also such a fiber.

The most used vegetable fibers are cotton, flax and hemp, although sisal, jute, kenaf, bamboo and coconut are also widely used.

Hemp fibers are mainly used for ropes and aerofoils because of their high suppleness and resistance within an aggressive environment. Hemp fibers are, for example, currently used as a seal within the heating and sanitary industries.

Animal fibers

Animal fibers generally comprise proteins such as collagen and keratin; examples include silk, sinew, wool, catgut, angora, mohair and alpaca.

- Animal hair (wool or hairs): Fiber or wool taken from animals or hairy mammals. e.g. sheep's wool, goat hair (cashmere, mohair), alpaca hair, horse hair, etc.
- Silk fiber: Fiber collected from dried saliva of bugs or insects during the preparation of cocoons.
- Avian fiber: Fibers from birds, e.g. feathers and feather fiber.

Industrial usage

After World War II, the build-up of synthetic fibers significantly decreased the use of natural fibers. Now, with the increase of oil prices and environmental considerations, there has been a revival of natural fiber use within the textile, building, plastic and automotive industries. This interest is reinforced by the developmental perspectives on the agro-industrial market and local productions, allowing economic development and independence versus imported materials.

France remains the greatest European hemp fiber producer with 50,000 tons yearly (EU 100,000 tons). France also produces the largest range of industrial seeds worldwide. China and Russia are also important producers, but the statistics in that field are not available.

In the industrial domain, the consortium DAIFA group SAS have reached a leading position in Europe in the automotive plastics market. They specialize in injection and thermopress plastics reinforced with natural fibers.

The use of natural fibers at the industrial level improves the environmental sustainability of the parts being constructed, especially within the automotive market. Within the building industry, the interest in natural fibers is mostly economical and technical; natural fibers allow insulation properties higher than current materials.

Synthetic fiber

Synthetic fibers are the result of extensive research by scientists to improve on naturally occurring animal and plant fibers. In general, synthetic fibers are created by forcing, usually through extrusion, fiber forming materials through holes (called spinnerets) into the air, forming a thread. Before synthetic fibers were developed, artificially manufactured fibers were made from cellulose, which comes from plants. These fibers are called cellulose fibers.

Synthetic fibers account for about half of all fiber usage, with applications in every field of fiber and textile technology. Although many classes of fiber based on synthetic polymers have been evaluated as potentially valuable commercial products, four of them - nylon, polyester, acrylic and polyolefin - dominate the market. These four account for approximately 98 per cent by volume of synthetic fiber production, with polyester alone accounting for around 60 per cent.

History

The first artificial fiber, known as artificial silk, became known as viscose around 1894, and finally rayon in 1924. A similar product known as cellulose acetate was discovered in 1865. Rayon and acetate are both artificial fibers, but not truly synthetic, being made from wood. Although these artificial fibers were discovered in the mid-nineteenth century, successful modern manufacture began much later.

Nylon, the first synthetic fiber, made its debut in the United States as a replacement for silk, just in time for World War II rationing. Its novel use as a material for women's stockings overshadowed more practical uses, such as a replacement for the silk in parachutes and other military uses.

Common synthetic fibers include:

- Rayon (1910) (artificial, not synthetic)
- Acetate (1924) (artificial, not synthetic)
- Nylon (1939)
- Modacrylic (1949)
- Olefin (1949)
- Acrylic (1950)
- Polyester (1953)
- Carbon fiber (1968)

Specialty synthetic fibers include:

- Vinyon (1939)
- Saran (1941)
- Spandex (1959)
- Sulfar (1983)
- Lyocell (1992)
- PLA (2002)

- Vinalon (1939)
- Aramids (1961) - known as Nomex, Kevlar and Twaron
- Modal (1960's)
- Dyneema/Spectra (1979)
- PBI (Polybenzimidazole fiber) (1983)
- M-5 (PIPD fiber)
- Orlon
- Zylon (PBO fiber)
- Vectran (TLCP fiber) made from Vectra LCP polymer
- Derclon used in manufacture of rugs

Other synthetic materials used in fibers include:

- Acrylonitrile rubber (1930)

Modern fibers that are made from older artificial materials include:

- Glass Fiber (1938) is used for:
  - industrial, automotive, and home insulation (Glass wool)
  - reinforcement of composite materials (Glass-reinforced plastic, Glass fiber reinforced concrete)
  - specialty papers in battery separators and filtration
- Metallic fiber (1946) is used for:
  - adding metallic properties to clothing for the purpose of fashion (usually made with composite plastic and metal foils)
  - elimination and prevention of static charge build-up
  - conducting electricity to transmit information
  - conduction of heat

In the horticulture industry synthetics are often used in soils to help the plants grow better. Examples are:

- expanded polystyrene flakes
- urea-formaldehyde foam resin
- polyurethane foam
- phenolic resin foam

Chapter- 3

Glass (fiber)

Bundle of fiberglass

Fiberglass, (also called **fibreglass** and **glass fibre**), is a material consisting of numerous extremely fine fibers of glass.

Glassmakers throughout history have experimented with glass fibers, but mass manufacture of fiberglass was only made possible with the invention of finer machine tooling. In 1893, Edward Drummond Libbey exhibited a dress at the World's Columbian Exposition incorporating glass fibers with the diameter and texture of silk fibers. This was first worn by the popular stage actress of the time Georgia Cayvan.

Glass wool, which is commonly known as "fiberglass" today, however, was invented in 1938 by Russell Games Slayter of Owens-Corning as a material to be used as insulation. It is marketed under the trade name **Fiberglas,** which has become a genericized trademark.

Fiberglass is commonly used as an insulating material. It is also used as a reinforcing agent for many polymer products; the resulting composite material, properly known as fiber-reinforced polymer (FRP) or glass-reinforced plastic (GRP), is also called "fiberglass" in popular usage.

A somewhat similar, but more expensive technology used for applications requiring very high strength and low weight is the use of carbon fiber.

Fiber formation

Glass fiber is formed when thin strands of silica-based or other formulation glass is extruded into many fibers with small diameters suitable for textile processing. The technique of heating and drawing glass into fine fibers has been known for millennia; however, the use of these fibers for textile applications is more recent. Until this time all fiberglass had been manufactured as staple (a term used to describe naturally formed clusters or locks of wool fibres). The first commercial production of fiberglass was in 1936. In 1938 Owens-Illinois Glass Company and Corning Glass Works joined to form the Owens-Corning Fiberglas Corporation. When the two companies joined to produce and promote fiberglass, they introduced continuous filament glass fibers. Owens-Corning is still the major fiberglass producer in the market today.

The types of fiberglass most commonly used are mainly E-glass (alumino-borosilicate glass with less than 1 wt% alkali oxides, mainly used for glass-reinforced plastics), but also A-glass (alkali-lime glass with little or no boron oxide), E-CR-glass (alumino-lime silicate with less than 1 wt% alkali oxides, has high acid resistance), C-glass (alkali-lime glass with high boron oxide content, used for example for glass staple fibers), D-glass (borosilicate glass with high dielectric constant), R-glass (alumino silicate glass without MgO and CaO with high mechanical requirements), and S-glass (alumino silicate glass without CaO but with high MgO content with high tensile strength).

Chemistry

Although pure silica is a perfectly viable glass and glass fiber, it must be worked with at very high temperatures, which is a drawback unless its specific chemical properties are needed. It is usual to introduce impurities into the glass in the form of other materials to lower its working temperature. These materials also impart various other properties to the glass that may be beneficial in different applications. The first type of glass used for fiber was soda lime glass or A glass. It was not very resistant to alkali. A new type, E-glass, was formed; this is an alumino-borosilicate glass that is alkali free (<2%). This was the first glass formulation used for continuous filament formation. E-glass still makes up most of the fiberglass production in the world. Its particular components may differ slightly in percentage, but must fall within a specific range. The letter E is used because it was originally for electrical applications. S-glass is a high-strength formulation for use when tensile strength is the most important property. C-glass was developed to resist attack from chemicals, mostly acids that destroy E-glass. T-glass is a North American variant of C-glass. A-glass is an industry term for cullet glass, often bottles, made into fiber. AR-glass is alkali-resistant glass. Most glass fibers have limited solubility in water but are very dependent on pH. Chloride ions will also attack and dissolve E-glass surfaces.

Since E-glass does not really melt, but soften, the softening point is defined as "the temperature at which a 0.55–0.77 mm diameter fiber 235 mm long, elongates under its own weight at 1 mm/min when suspended vertically and heated at the rate of 5°C per minute". The strain point is reached when the glass has a viscosity of $10^{14.5}$ poise. The annealing point, which is the temperature where the internal stresses are reduced to an acceptable commercial limit in 15 minutes, is marked by a viscosity of 10^{13} poise.

Properties

Thermal

Glass fibers are useful because of their high ratio of surface area to weight. However, the increased surface area makes them much more susceptible to chemical attack. By trapping air within them, blocks of glass fiber make good thermal insulation, with a thermal conductivity of the order of 0.05 W/(m·K).

Tensile

Fiber type	Tensile strength (MPa)	Density (g/cm^3)
E-Glass	3,450	2.57
S-Glass	4,710	2.48

The strength of glass is usually tested and reported for "virgin" or pristine fibers—those that have just been manufactured. The freshest, thinnest fibers are the strongest because the thinner fibers are more ductile. The more the surface is scratched, the less the resulting tenacity. Because glass has an amorphous structure, its properties are the same along the fiber and across the fiber. Humidity is an important factor in the tensile strength. Moisture is easily adsorbed, and can worsen microscopic cracks and surface defects, and lessen tenacity.

In contrast to carbon fiber, glass can undergo more elongation before it breaks. There is a correlation between bending diameter of the filament and the filament diameter. The viscosity of the molten glass is very important for manufacturing success. During drawing (pulling of the glass to reduce fiber circumference), the viscosity should be relatively low. If it is too high, the fiber will break during drawing. However, if it is too low, the glass will form droplets rather than drawing out into fiber.

Safety

Fiberglass has increased in popularity since the discovery that asbestos causes cancer and its subsequent removal from most products. However, the safety of fiberglass is also being called into question, as research shows that the composition of this material (asbestos and fiberglass are both silicate fibers) causes similar toxicity as asbestos.

1970s studies on rats found that fibrous glass of less than 3 micrometers in diameter and greater than 20 micrometers in length is a "potent carcinogen". Likewise, the International Agency for Research on Cancer found it "may reasonably be anticipated to be a carcinogen" in 1990. The American Conference of Governmental Industrial Hygienists, on the other hand, says that there is insufficient evidence, and that fiberglass is in group A4: "Not classifiable as a human carcinogen".

The North American Insulation Manufacturers Association (NAIMA) claims that fiberglass is fundamentally different from asbestos, since it is man-made instead of naturally-occurring. They claim that fiberglass "dissolves in the lungs", while asbestos remains in the body for life. Although both fiberglass and asbestos are made from silica filaments, NAIMA claims that asbestos is more dangerous because of its crystalline structure, which causes it to cleave into smaller, more dangerous pieces, citing the U.S. Department of Health and Human Services:

Synthetic vitreous fibers [fiber glass] differ from asbestos in two ways that may provide at least partial explanations for their lower toxicity. Because most synthetic vitreous fibers are not crystalline like asbestos, they do not split longitudinally to form thinner fibers. They also generally have markedly less biopersistence in biological tissues than asbestos fibers because they can undergo dissolution and transverse breakage.

A 1998 rat study found that the biopersistence of synthetic fibers after one year was 0.04–10%, but 27% for amosite asbestos. Fibers that persisted longer were found to be more carcinogenic.

Glass-reinforced plastic

Glass-reinforced plastic (GRP) is a composite material or fiber-reinforced plastic made of a plastic reinforced by fine glass fibers. Like graphite-reinforced plastic, the composite material is commonly referred to by the name of its reinforcing fibers (fiberglass). Thermosetting plastics are normally used for GRP production—most often unsaturated polyester (using 2-butanone peroxide aka MEK peroxide as a catalyst), but vinylester or epoxy are also used. Traditionally, styrene monomer was used as a reactive diluent in the resin formulation giving the resin a characteristic odor. More recently alternatives have been developed. The glass can be in the form of a chopped strand mat (CSM) or a woven fabric.

As with many other composite materials (such as reinforced concrete), the two materials act together, each overcoming the deficits of the other. Whereas the plastic resins are strong in compressive loading and relatively weak in tensile strength, the glass fibers are very strong in tension but have no strength against compression. By combining the two materials, GRP becomes a material that resists both compressive and tensile forces well. The two materials may be used uniformly or the glass may be specifically placed in those portions of the structure that will experience tensile loads.

Uses

Uses for regular fiberglass include mats, thermal insulation, electrical insulation, sound insulation, reinforcement of various materials, tent poles, sound absorption, heat- and corrosion-resistant fabrics, high-strength fabrics, pole vault poles, arrows, bows and crossbows, translucent roofing panels, automobile bodies, hockey sticks, surfboards, boat hulls, and paper honeycomb. It has been used for medical purposes in casts. Fiberglass is extensively used for making FRP tanks and vessels. Fiberglass is also used in the design of Irish stepdance shoes.

Role of recycling in fiberglass manufacturing

Manufacturers of fiberglass insulation can use recycled glass. Owens Corning's fiberglass has 40% recycled glass. A recycling program begun in 2009 in Kansas City, Kansas, will ship crushed recycled glass, called cullet, to the Owens Corning plant that will use it as raw material for fiberglass making.

Chapter- 4

Carbon Fiber-reinforced Polymer

Tail of an RC helicopter, made of CFRP

Carbon fiber-reinforced polymer or **carbon fiber-reinforced plastic** (**CFRP** or **CRP**), is a very strong, light, and expensive composite material or fiber-reinforced polymer. Similar to fiberglass (glass reinforced polymer), the composite material is commonly referred to by the name of its reinforcing fibers (carbon fiber). The polymer is most often epoxy, but other polymers, such as polyester, vinyl ester or nylon, are sometimes used. Some composites contain both carbon fiber and other fibers such as Kevlar, aluminium, and fiberglass reinforcement. The terms **graphite-reinforced polymer** or **graphite fiber-reinforced polymer** (**GFRP**) are also used, but less commonly, since glass-(fiber)-reinforced polymer can also be called GFRP. In product advertisements, it is sometimes referred to simply as **graphite fiber** (or **graphite fibre**), for short.

It has many applications in aerospace and automotive fields, as well as in sailboats, and notably in modern bicycles and motorcycles, where its high strength-to-weight ratio is of importance. Improved manufacturing techniques are reducing the costs and time to manufacture, making it increasingly common in small consumer goods as well, such as laptops, tripods, fishing rods, paintball equipment, archery equipment, racquet frames, stringed instrument bodies, classical guitar strings, drum shells, golf clubs, and pool/billiards/snooker cues.

Composite

Materials produced with the above-mentioned methodology are often generically referred to as *composites*. The choice of matrix can have a profound effect on the properties of the finished composite. One method of producing graphite-epoxy parts is by layering sheets of carbon fiber cloth into a mold in the shape of the final product. The alignment and weave of the cloth fibers is chosen to optimize the strength and stiffness properties of the resulting material. The mold is then filled with epoxy and is heated or air-cured. The resulting part is very corrosion-resistant, stiff, and strong for its weight. Parts used in less critical areas are manufactured by draping cloth over a mold, with epoxy either preimpregnated into the fibers (also known as *prepreg*) or "painted" over it. High-performance parts using single molds are often vacuum-bagged and/or autoclave-cured, because even small air bubbles in the material will reduce strength.

Process

The process by which most carbon fiber-reinforced polymer is made varies, depending on the piece being created, the finish (outside gloss) required, and how many of this particular piece are going to be produced.

For simple pieces of which relatively few copies are needed, (1–2 per day) a vacuum bag can be used. A fiberglass, carbon fiber or aluminum mold is polished and waxed, and has a release agent applied before the fabric and resin are applied, and the vacuum is pulled and set aside to allow the piece to cure (harden). There are two ways to apply the resin to the fabric in a vacuum mold. One is called a wet layup, where the two-part resin is mixed and applied before being laid in the mold and placed in the bag. The other is a resin induction system, where the dry fabric and mold are placed inside the bag while the vacuum pulls the resin through a small tube into the bag, then through a tube with holes or something similar to evenly spread the resin throughout the fabric. Wire loom works perfectly for a tube that requires holes inside the bag. Both of these methods of applying resin require hand work to spread the resin evenly for a glossy finish with very small pin-holes. A third method of constructing composite materials is known as a dry layup. Here, the carbon fiber material is already impregnated with resin (prepreg) and is applied to the mold in a similar fashion to adhesive film. The assembly is then placed in a vacuum to cure. The dry layup method has the least amount of resin waste and can achieve lighter constructions than wet layup. Also, because larger amounts of resin are more difficult to bleed out with wet layup methods, prepreg parts generally have fewer pinholes. Pinhole elimination with minimal resin amounts generally require the use of autoclave pressures to purge the residual gases out.

A quicker method uses a compression mold. This is a two-piece (male and female) mold usually made out of fiberglass or aluminum that is bolted together with the fabric and resin between the two. The benefit is that, once it is bolted together, it is relatively clean and can be moved around or stored without a vacuum until after curing. However, the molds require a lot of material to hold together through many uses under that pressure.

Many carbon fiber-reinforced polymer parts are created with a single layer of carbon fabric, and filled with fiberglass. A tool called a chopper gun can be used to quickly create these types of parts. Once a thin shell is created out of carbon fiber, the chopper gun is a pneumatic tool that cuts fiberglass from a roll and sprays resin at the same time, so that the fiberglass and resin are mixed on the spot. The resin is either external mix, wherein the hardener and resin are sprayed separately, or internal, where they are mixed internally, which requires cleaning after every use.

For difficult or convoluted shapes, a filament winder can be used to make pieces.

Automotive uses

Carbon fiber-reinforced polymer is used extensively in high-end automobile racing. The high cost of carbon fiber is mitigated by the material's unsurpassed strength-to-weight ratio, and low weight is essential for high-performance automobile racing. Racecar manufacturers have also developed methods to give carbon fiber pieces strength in a certain direction, making it strong in a load-bearing direction, but weak in directions where little or no load would be placed on the member. Conversely, manufacturers developed omnidirectional carbon fiber weaves that apply strength in all directions. This type of carbon fiber assembly is most widely used in the "safety cell" monocoque chassis assembly of high-performance racecars.

Many supercars over the past few decades have incorporated CFRP extensively in their manufacture, using it for their monocoque chassis as well as other components.

Until recently, the material has had limited use in mass-produced cars because of the expense involved in terms of materials, equipment, and the relatively limited pool of individuals with expertise in working with it. Recently, several mainstream vehicle manufacturers have started to use CFRP in everyday road cars.

Use of the material has been more readily adopted by low-volume manufacturers who used it primarily for creating body-panels for some of their high-end cars due to its increased strength and decreased weight compared with the glass-reinforced polymer they used for the majority of their products.

Civil engineering applications

Carbon fiber reinforced polymer-[CFRP] has over the past two decades become an increasingly notable material used in structural engineering applications. Studied in an academic context as to its potential benefits in construction, it has also proved itself cost-effective in a number of field applications strengthening concrete, masonry, steel, cast iron, and timber structures. Its use in industry can be either for retrofitting to strengthen an existing structure or as an alternative reinforcing (or prestressing material) instead of steel from the outset of a project.

Retrofitting has become the increasingly dominant use of the material in civil engineering, and applications include increasing the load capacity of old structures (such as bridges) that were designed to tolerate far lower service loads than they are experiencing today, seismic retrofitting, and repair of damaged structures. Retrofitting is popular in many instances as the cost of replacing the deficient structure can greatly exceed its strengthening using CFRP.

Applied to reinforced concrete structures for flexure, CFRP typically has a large impact on strength (doubling or more the strength of the section is not uncommon), but only a moderate increase in stiffness (perhaps a 10% increase). This is because the material used in this application is typically very strong (e.g., 3000 MPa ultimate tensile strength, more than 10 times mild steel) but not particularly stiff (150 to 250 GPa, a little less than steel, is typical). As a consequence, only small cross-sectional areas of the material are used. Small areas of very high strength but moderate stiffness material will significantly increase strength, but not stiffness.

CFRP can also be applied to enhance shear strength of reinforced concrete by wrapping fabrics or fibers around the section to be strengthened. Wrapping around sections (such as bridge or building columns) can also enhance the ductility of the section, greatly increasing the resistance to collapse under earthquake loading. Such 'seismic retrofit' is the major application in earthquake-prone areas, since it is much more economic than alternative methods.

If a column is circular (or nearly so) an increase in axial capacity is also achieved by wrapping. In this application, the confinement of the CFRP wrap enhances the compressive strength of the concrete. However, although large increases are achieved in the ultimate collapse load, the concrete will crack at only slightly enhanced load, meaning that this application is only occasionally used.

Specialist ultra-high modulus CFRP (with tensile modulus of 420 GPa or more) is one of the few practical methods of strengthening cast-iron beams. In typical use, it is bonded to the tensile flange of the section, both increasing the stiffness of the section and lowering the neutral axis, thus greatly reducing the maximum tensile stress in the cast iron.

When used as a replacement for steel, CFRP bars could be used to reinforce concrete structures, however the applications are not common.

CFRP could be used as prestressing materials due to their high strength. The advantages of CFRP over steel as a prestressing material, namely its light weight and corrosion resistance, should enable the material to be used for niche applications such as in offshore environments. However, there are practical difficulties in anchorage of carbon fiber strands and applications of this are rare.

In the United States, Prestressed Concrete Cylinder Pipes (PCCP) account for a vast majority of water transmission mains. Due to their large diameters, failures of PCCP are usually catastrophic and affect large populations. Approximately 19,000 miles of PCCP have been installed between 1940 and 2006. Corrosion in the form of hydrogen embrittlement has been blamed for the gradual deterioration of the prestressing wires in many PCCP lines. Over the past decade, CFRPs have been utilized to internally line PCCP, resulting in a fully structural strengthening system. Inside a PCCP line, the CFRP liner acts as a barrier that controls the level of strain experienced by the steel cylinder in the host pipe. The composite liner enables the steel cylinder to perform within its elastic range, to ensure the pipeline's long-term performance is maintained. CFRP liner designs are based on strain compatibility between the liner and host pipe.

CFRP is a more costly material than its counterparts in the construction industry, glass fiber-reinforced polymer (GFRP) and aramid fiber-reinforced polymer (AFRP), though CFRP is, in general, regarded as having superior properties.

Much research continues to be done on using CFRP both for retrofitting and as an alternative to steel as a reinforcing or prestressing material. Cost remains an issue and long-term durability questions still remain. Some are concerned about the brittle nature of CFRP, in contrast to the ductility of steel. Though design codes have been drawn up by institutions such as the American Concrete Institute, there remains some hesitation among the engineering community about implementing these alternative materials. In part, this is due to a lack of standardization and the proprietary nature of the fiber and resin combinations on the market, though this in itself is advantageous in that the material properties can be tailored to the desired application requirements.

Other applications

A carbon fiber and Kevlar canoe (Placid Boatworks Rapidfire at the Adirondack Canoe Classic)

Carbon fiber-reinforced polymer has found a lot of use in high-end sports equipment such as racing bicycles. For the same strength, a carbon-fiber frame weighs less than a bicycle tubing of aluminum or steel. The choice of weave can be carefully selected to maximize stiffness. The variety of shapes it can be built into has further increased stiffness and also allowed aerodynamic considerations into tube profiles. Carbon fiber-reinforced polymer frames, forks, handlebars, seatposts, and crank arms are becoming more common on medium- and higher-priced bicycles. Carbon fiber-reinforced polymer forks are used on most new racing bicycles. Other sporting goods applications include rackets, fishing rods, longboards, and rowing shells.

Much of the fuselage of the new Boeing 787 Dreamliner and Airbus A350 XWB will be composed of CFRP, making the aircraft lighter than a comparable aluminum fuselage, with the added benefit of less maintenance thanks to CFRP's superior fatigue resistance.

Due to its high ratio of strength to weight, CFRP is widely used in micro air vehicles (MAVs). In MAVSTAR Project, the CFRP structures reduce the weight of the MAV significantly. In addition, the high stiffness of the CFRP blades overcome the problem of collision between blades under strong wind.

CFRP has also found application in the construction of high-end audio components such as turntables and loudspeakers, again due to its stiffness.

It is used for parts in a variety of musical instruments, including violin bows, guitar pickguards, and a durable ebony replacement for bagpipe chanters. It is also used to create entire musical instruments such as Blackbird Guitars carbon fiber rider models, Luis and Clark carbon fiber cellos, and Mix carbon fiber mandolins.

In firearms it can substitute for metal, wood, and fiberglass in many areas of a firearm in order to reduce overall weight. However, while it is possible to make the receiver out of synthetic material such as carbon fiber, many of the internal parts are still limited to metal alloys as current reinforced plastics are unsuitable replacements.

Shoe manufacturers use carbon fiber as a shank plate in their basketball sneakers to keep the foot stable. It usually runs the length of the sneaker just above the sole and is left exposed in some areas, usually in the arch of the foot.

CFRP is used, either as standard equipment or in aftermarket parts, in high-performance radio-controlled vehicles and aircraft, i.a. for the main rotor blades of radio controlled helicopters—which should be light and stiff to perform 3D maneuvers.

Fire resistance of polymers or thermoset composites is significantly improved if a thin layer of carbon fibers is molded near the surface—dense, compact layer of carbon fibers efficiently reflects heat.

Covers of Thinkpads laptops from Lenovo/IBM and Sony use this technology.

Carbon fiber is a popular material to form the handles of high-end knives.

This material is used when manufacturing squash, tennis and badminton racquets.

Carbon-Graphite spars are used on the frames of high-end Sport kites

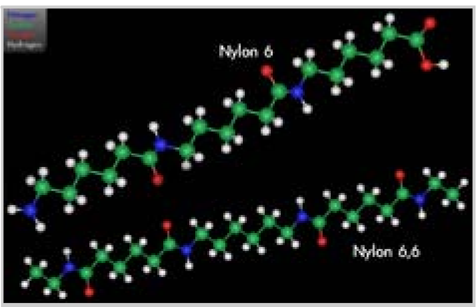
In 2006 Kookaburra Sport introduced cricket bats with a thin carbon fibre layer on the back which were endorsed and used in competitive matches by high-profile players including Ricky Ponting and Michael Hussey. The carbon fibre was claimed to increase the durability of the bats, however they were banned from all first-class matches by the ICC in 2007.

End of useful life/recycling

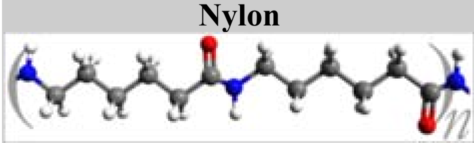
Carbon fiber-reinforced polymers (CFRPs) have an almost infinite service lifetime when protected from the sun, and, unlike steel alloys, have no endurance limit when exposed to cyclic loading. When it is time to decommission CFRPs, they cannot be melted down in air like many metals. When free of vinyl (PVC or polyvinyl chloride) and other halogenated polymers, CFRPs can be thermally decomposed via thermal depolymerization in an oxygen-free environment. This can be accomplished in a refinery in a one-step process. Capture and reuse of the carbon and monomers is then possible. CFRPs can also be milled or shredded at low temperature to reclaim the carbon fiber, however this process shortens the fibers dramatically. Just as with downcycled paper, the shortened fibers cause the recycled material to be weaker than the original material. There are still many industrial applications that do not need the strength of full-length carbon fiber reinforcement. For example, chopped reclaimed carbon fiber can be used in consumer electronics, such as laptops. It provides excellent reinforcement of the polymers used even if it lacks the strength-to-weight ratio of an aerospace component.

Chapter- 5

Nylon



Nylon



Density	1.15 g/cm^3
Electrical conductivity (σ)	10^{-12} S/m
Thermal conductivity	0.25 W/(m·K)
Melting point	463–624 K 190–350 °C 374–663 °F

Nylon is a generic designation for a family of synthetic polymers known generically as polyamides, first produced on February 28, 1935, by Wallace Carothers at DuPont's research facility at the DuPont Experimental Station. Nylon is one of the most commonly used polymers.

Overview

Nylon is a thermoplastic silky material, first used commercially in a nylon-bristled toothbrush (1938), followed more famously by women's stockings ("nylons"; 1940). It is made of repeating units linked by amide bonds and is frequently referred to as *polyamide*

(PA). Nylon was the first commercially successful synthetic polymer. There are two common methods of making nylon for fiber applications. In one approach, molecules with an acid (COOH) group on each end are reacted with molecules containing amine (NH_2) groups on each end. The resulting nylon is named on the basis of the number of carbon atoms separating the two acid groups and the two amines. These are formed into monomers of intermediate molecular weight, which are then reacted to form long polymer chains.

Nylon was intended to be a synthetic replacement for silk and substituted for it in many different products after silk became scarce during World War II. It replaced silk in military applications such as parachutes and flak vests, and was used in many types of vehicle tires.

Nylon fibres are used in many applications, including fabrics, bridal veils, carpets, musical strings, and rope.

Solid nylon is used for mechanical parts such as machine screws, gears and other low- to medium-stress components previously cast in metal. Engineering-grade nylon is processed by extrusion, casting, and injection molding. Solid nylon is used in hair combs. Type 6,6 Nylon 101 is the most common commercial grade of nylon, and Nylon 6 is the most common commercial grade of molded nylon. Nylon is available in glass-filled variants which increase structural and impact strength and rigidity, and molybdenum sulfide-filled variants which increase lubricity.

Aramids are another type of polyamide with quite different chain structures which include aromatic groups in the main chain. Such polymers make excellent ballistic fibres.

Chemistry

Nylons are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid, so that amides are formed at both ends of each monomer in a process analogous to polypeptide biopolymers. Chemical elements included are carbon, hydrogen, nitrogen, and oxygen. The numerical suffix specifies the numbers of carbons donated by the monomers; the diamine first and the diacid second. The most common variant is nylon 6-6 which refers to the fact that the diamine (hexamethylene diamine, IUPAC name: 1,6-diaminohexane) and the diacid (adipic acid, IUPAC name: hexane-1,6-dicarboxylic acid) each donate 6 carbons to the polymer chain. As with other regular copolymers like polyesters and polyurethanes, the "repeating unit" consists of one of each monomer, so that they alternate in the chain. Since each monomer in this copolymer has the same reactive group on both ends, the direction of the amide bond reverses between each monomer, unlike natural polyamide proteins which have overall directionality: C terminal → N terminal. In the laboratory, nylon 6-6 can also be made using adipoyl chloride instead of adipic.

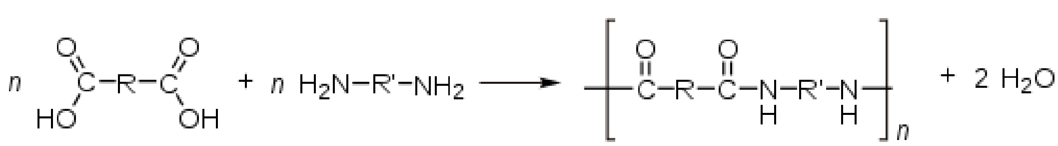
It is difficult to get the proportions exactly correct, and deviations can lead to chain termination at molecular weights less than a desirable 10,000 daltons (u). To overcome this problem, a crystalline, solid "nylon salt" can be formed at room temperature, using an exact 1:1 ratio of the acid and the base to neutralize each other. Heated to 285 °C (545 °F), the salt reacts to form nylon polymer. Above 20,000 daltons, it is impossible to spin the chains into yarn, so to combat this, some acetic acid is added to react with a free amine end group during polymer elongation to limit the molecular weight. In practice, and especially for 6,6, the monomers are often combined in a water solution. The water used to make the solution is evaporated under controlled conditions, and the increasing concentration of "salt" is polymerized to the final molecular weight.

DuPont patented nylon 6,6, so in order to compete, other companies (particularly the German BASF) developed the homopolymer nylon 6, or polycaprolactam — not a condensation polymer, but formed by a ring-opening polymerization (alternatively made by polymerizing aminocaproic acid). The peptide bond within the caprolactam is broken with the exposed active groups on each side being incorporated into two new bonds as the monomer becomes part of the polymer backbone. In this case, all amide bonds lie in the same direction, but the properties of nylon 6 are sometimes indistinguishable from those of nylon 6,6 — except for melt temperature and some fiber properties in products like carpets and textiles. There is also nylon 9.

The 428 °F (220 °C) melting point of nylon 6 is lower than the 509 °F (265 °C) melting point of nylon 6,6.

Nylon 5,10, made from pentamethylene diamine and sebacic acid, was studied by Carothers even before nylon 6,6 and has superior properties, but is more expensive to make. In keeping with this naming convention, "nylon 6,12" (N-6,12) or "PA-6,12" is a copolymer of a 6C diamine and a 12C diacid. Similarly for N-5,10 N-6,11; N-10,12, etc. Other nylons include copolymerized dicarboxylic acid/diamine products that are *not* based upon the monomers listed above. For example, some aromatic nylons are polymerized with the addition of diacids like terephthalic acid (→ Kevlar Twaron) or isophthalic acid (→ Nomex), more commonly associated with polyesters. There are copolymers of N-6,6/N6; copolymers of N-6,6/N-6/N-12; and others. Because of the way polyamides are formed, nylon would seem to be limited to unbranched, straight chains. But "star" branched nylon can be produced by the condensation of dicarboxylic acids with polyamines having three or more amino groups.

The general reaction is:



A molecule of water is given off and the nylon is formed. Its properties are determined by the R and R' groups in the monomers. In nylon 6,6, R = 4C and R' = 6C alkanes, but one also has to include the two carboxyl carbons in the diacid to get the number it donates to the chain. In Kevlar, both R and R' are benzene rings.

Concepts of nylon production

The first approach: combining molecules with an acid (COOH) group on each end are reacted with two chemicals that contain amine (NH_2) groups on each end. This process creates nylon 6,6, made of hexamethylene diamine with six carbon atoms and adipic acid.

The second approach: a compound has an acid at one end and an amine at the other and is polymerized to form a chain with repeating units of $(-NH-[CH_2]_n-CO-)_x$. In other words, nylon 6 is made from a single six-carbon substance called caprolactam. In this equation, if n=5, then nylon 6 is the assigned name (may also be referred to as polymer).

The characteristic features of nylon 6,6 include:

- Pleats and creases can be heat-set at higher temperatures
- More compact molecular structure
- Better weathering properties; better sunlight resistance
- Softer "Hand"
- Higher melting point (256 °C / 492.8 °F)
- Superior colorfastness
- Excellent abrasion resistance

On the other hand, nylon 6 is easy to dye, more readily fades; it has a higher impact resistance, a more rapid moisture absorption, greater elasticity and elastic recovery.

Characteristics

- Variation of luster: nylon has the ability to be very lustrous, semilustrous or dull.
- Durability: its high tenacity fibers are used for seatbelts, tire cords, ballistic cloth and other uses.
- High elongation
- Excellent abrasion resistance
- Highly resilient (nylon fabrics are heat-set)
- Paved the way for easy-care garments
- High resistance to insects, fungi, animals, as well as molds, mildew, rot and many chemicals
- Used in carpets and nylon stockings
- Melts instead of burning
- Used in many military applications
- Good specific strength
- Transparent under infrared light (-12dB)

Bulk properties

Above their melting temperatures, T_m, thermoplastics like nylon are amorphous solids or viscous fluids in which the chains approximate random coils. Below T_m, amorphous regions alternate with regions which are lamellar crystals. The amorphous regions contribute elasticity and the crystalline regions contribute strength and rigidity. The planar amide (-CO-NH-) groups are very polar, so nylon forms multiple hydrogen bonds among adjacent strands. Because the nylon backbone is so regular and symmetrical, especially if all the amide bonds are in the *trans* configuration, nylons often have high crystallinity and make excellent fibers. The amount of crystallinity depends on the details of formation, as well as on the kind of nylon. Apparently it can never be quenched from a melt as a completely amorphous solid.

Nylon 6,6 can have multiple parallel strands aligned with their neighboring peptide bonds at coordinated separations of exactly 6 and 4 carbons for considerable lengths, so the carbonyl oxygens and amide hydrogens can line up to form interchain hydrogen bonds repeatedly, without interruption. Nylon 5,10 can have coordinated runs of 5 and 8 carbons. Thus parallel (but not antiparallel) strands can participate in extended, unbroken, multi-chain β-pleated sheets, a strong and tough supermolecular structure similar to that found in natural silk fibroin and the β-keratins in feathers. (Proteins have only an amino acid α-carbon separating sequential -CO-NH- groups.) Nylon 6 will form uninterrupted H-bonded sheets with mixed directionalities, but the β-sheet wrinkling is somewhat different. The three-dimensional disposition of each alkane hydrocarbon chain depends on rotations about the 109.47° tetrahedral bonds of singly-bonded carbon atoms.

When extruded into fibers through pores in an industrial spinneret, the individual polymer chains tend to align because of viscous flow. If subjected to cold drawing afterwards, the fibers align further, increasing their crystallinity, and the material acquires additional tensile strength. In practice, nylon fibers are most often drawn using heated rolls at high speeds.

Block nylon tends to be less crystalline, except near the surfaces due to shearing stresses during formation. Nylon is clear and colorless, or milky, but is easily dyed. Multistranded nylon cord and rope is slippery and tends to unravel. The ends can be melted and fused with a heat source such as a flame or electrode to prevent this.

When dry, polyamide is a good electrical insulator. However, polyamide is hygroscopic. The absorption of water will change some of the material's properties such as its electrical resistance. Nylon is less absorbent than wool or cotton.

Historical uses

Bill Pittendreigh, 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 the remaining 20%. By August 1945, manufactured fibers had taken a market share of 25% and cotton had dropped.

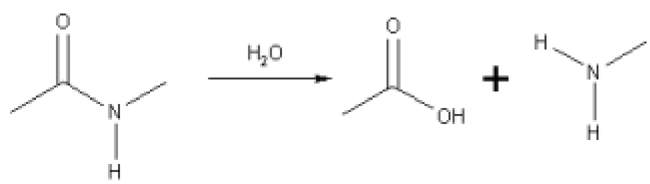
Some of the terpolymers based upon nylon are used every day in packaging. Nylon has been used for meat wrappings and sausage sheaths.

Use in composites

Nylon can be used as the matrix material in composite materials, with reinforcing fibres like glass or carbon fiber; such a composite has a higher density than pure nylon. Such thermoplastic composites (25% glass fibre) are frequently used in car components next to the engine, such as intake manifolds, where the good heat resistance of such materials makes them feasible competitors to metals.

Hydrolysis and degradation

All nylons are susceptible to hydrolysis, especially by strong acids, a reaction essentially the reverse of the synthetic reaction shown above. The molecular weight of nylon products so attacked drops fast, and cracks form quickly at the affected zones. Lower members of the nylons (such as nylon 6) are affected more than higher members such as nylon 12. This means that nylon parts cannot be used in contact with sulfuric acid for example, such as the electrolyte used in lead-acid batteries. When being molded, nylon must be dried to prevent hydrolysis in the molding machine barrel since water at high temperatures can also degrade the polymer. The reaction is of the type:



Incineration and recycling

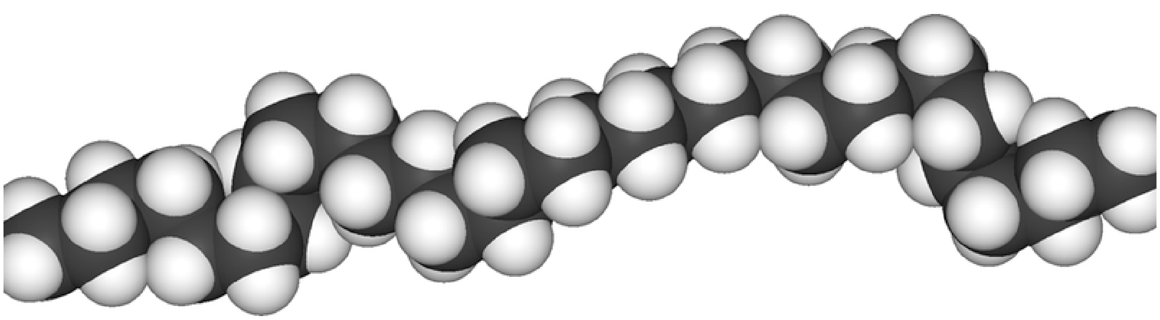
Various nylons break down in fire and form hazardous smoke, and toxic fumes or ash, typically containing hydrogen cyanide. Incinerating nylons to recover the high energy used to create them is usually expensive, so most nylons reach the garbage dumps, decaying very slowly. Some recycling is done on nylon, usually creating pellets for reuse in the industry, but this is done at a much lower scale.

Chapter- 6

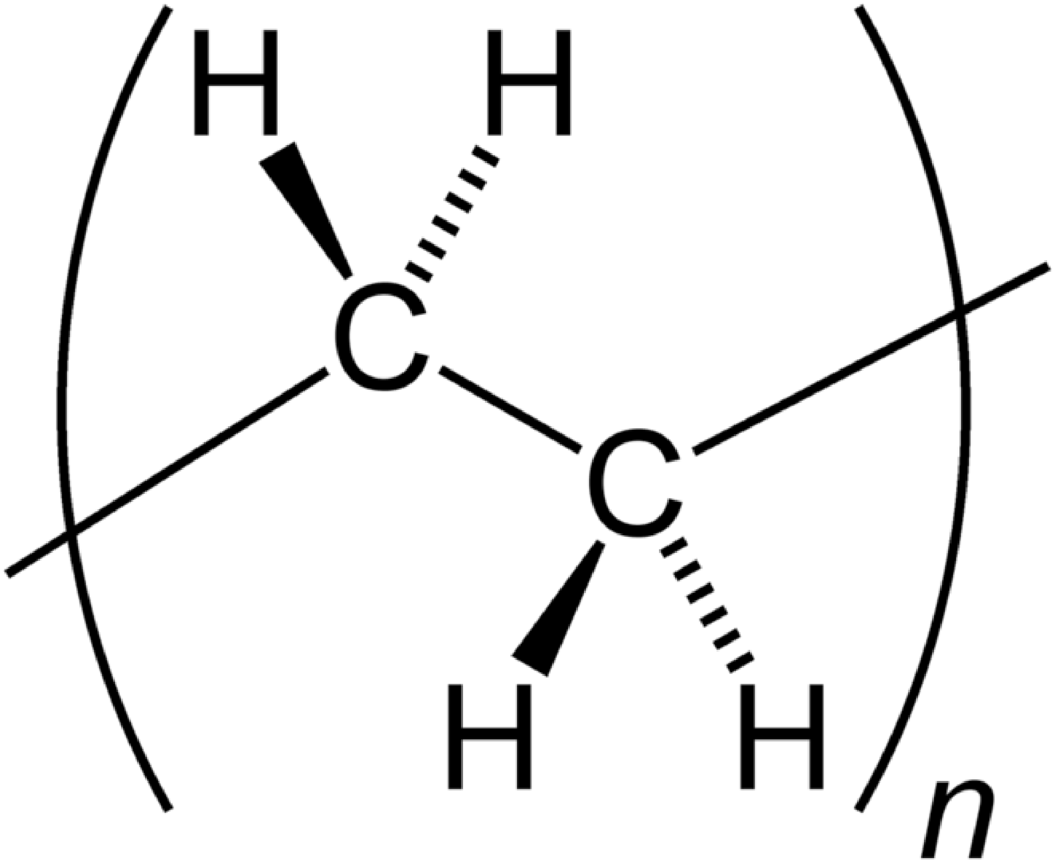
Polyethylene

Granulated polyethylene

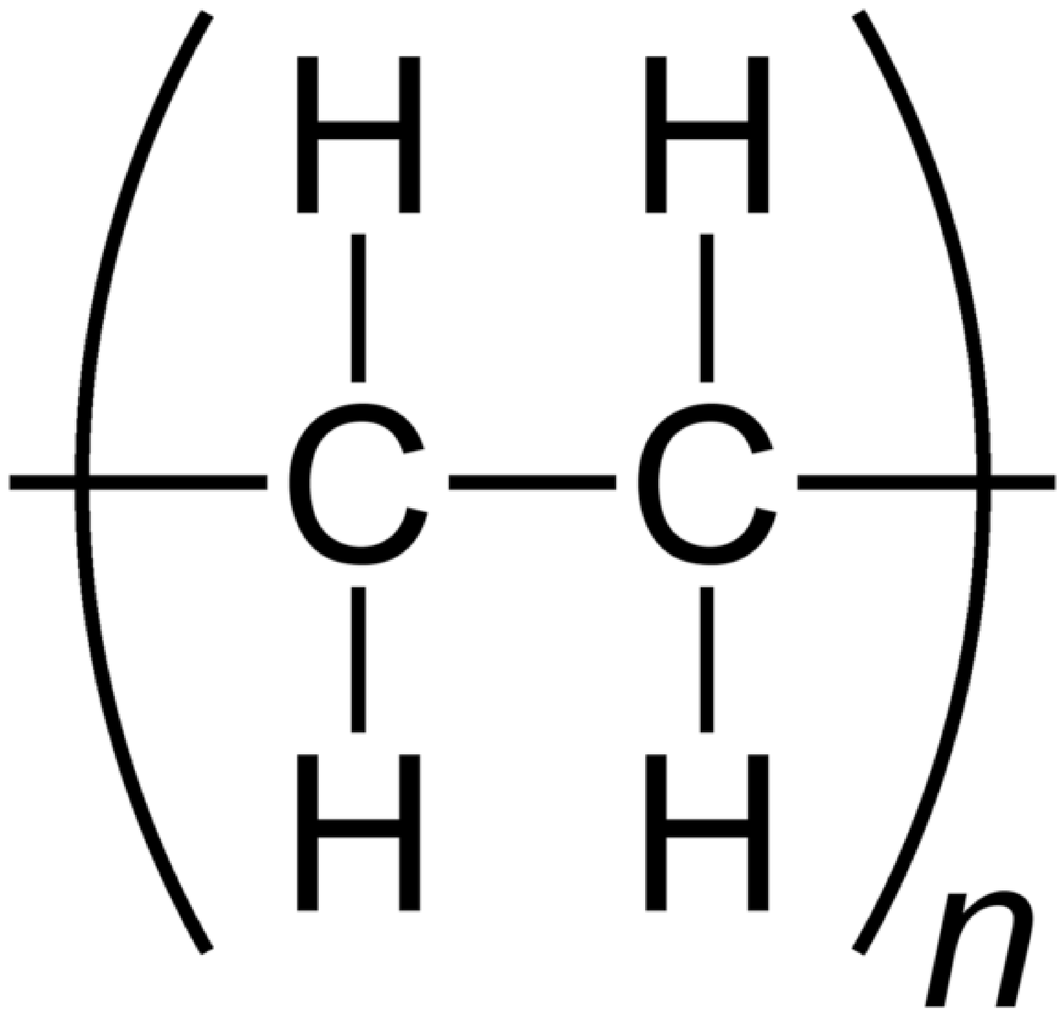
A bag manufactured from polyethylene



Space-filling model of a **polyethylene** chain



The repeating unit of **polyethylene**, showing its stereochemistry



A simpler way of representing the repeating unit. Note, however, that the C−H bond angles are not 90° as this diagram would indicate, but are approximately 110°, since each carbon atom is tetrahedral (sp^3).

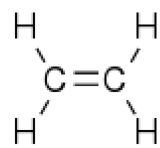
Polyethylene or **polythene** (IUPAC name **polyethene** or **poly(methylene)**) is the most widely used plastic, with an annual production of approximately 80 million metric tons. Its primary use is within packaging (plastic bag, etc.).

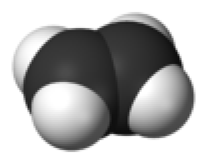
Description

Polyethylene is a thermoplastic polymer consisting of long chains produced by combing the ingredient monomer ethylene (IUPAC name ethene), the name comes from the ingredient and not the actual chemical resulting. The ethylene actually converts to ethane as it takes its place in a polymer and straight sections of the polymer are the same structure as the simple chain hydrocarbons, e.g., propane, decane and other straight single-bonded carbon chains. As with any polymer, the structure of the resulting substance defies molecular description due to cross branching of the chains. The recommended scientific name *polyethene* is systematically derived from the scientific name of the monomer. In certain circumstances it is useful to use a structure-based nomenclature; in such cases IUPAC recommends *poly(methylene)* (poly(methanediyl) is an non-preferred alternative). The difference in names between the two systems is due to the *opening up* of the monomer's double bond upon polymerization.

The name is abbreviated to **PE** in a manner similar to that by which other polymers like polypropylene and polystyrene are shortened to PP and PS respectively. In the United Kingdom the polymer is commonly called **polythene**, although this is not recognized scientifically.

The ethene molecule (known almost universally by its common name ethylene) C_2H_4 is CH_2=CH_2, Two CH_2 groups connected by a double bond, thus:





Polyethylene contains the chemical elements carbon and hydrogen.

Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene.

Classification

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. With regard to sold volumes, the most important polyethylene grades are HDPE, LLDPE and LDPE.

- Ultra high molecular weight polyethylene (UHMWPE)
- Ultra low molecular weight polyethylene (ULMWPE or PE-WAX)
- High molecular weight polyethylene (HMWPE)
- High density polyethylene (HDPE)
- High density cross-linked polyethylene (HDXLPE)
- Cross-linked polyethylene (PEX or XLPE)
- Medium density polyethylene (MDPE)
- Linear low density polyethylene (LLDPE)
- Low density polyethylene (LDPE)

- Very low density polyethylene (VLDPE)

UHMWPE is polyethylene with a molecular weight numbering in the millions, usually between 3.1 and 5.67 million. The high molecular weight makes it a very tough material, but results in less efficient packing of the chains into the crystal structure as evidenced by densities of less than high density polyethylene (for example, 0.930–0.935 g/cm^3). UHMWPE can be made through any catalyst technology, although Ziegler catalysts are most common. Because of its outstanding toughness and its cut, wear and excellent chemical resistance, UHMWPE is used in a diverse range of applications. These include can and bottle handling machine parts, moving parts on weaving machines, bearings, gears, artificial joints, edge protection on ice rinks and butchers' chopping boards. It competes with Aramid in bulletproof vests, under the tradenames Spectra and Dyneema, and is commonly used for the construction of articular portions of implants used for hip and knee replacements.

HDPE is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. The lack of branching is ensured by an appropriate choice of catalyst (for example, chromium catalysts or Ziegler-Natta catalysts) and reaction conditions. HDPE is used in products and packaging such as milk jugs, detergent bottles, margarine 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.

PEX is a medium- to high-density polyethylene containing cross-link bonds introduced into the polymer structure, changing the thermoplast into an elastomer. The high-temperature properties of the polymer are improved, its flow is reduced and its chemical resistance is enhanced. PEX is used in some potable-water plumbing systems because tubes made of the material can be expanded to fit over a metal nipple and it will slowly return to its original shape, forming a permanent, water-tight, connection.

MDPE is defined by a density range of 0.926–0.940 g/cm^3. MDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. MDPE has good shock and drop resistance properties. It also is less notch sensitive than HDPE, stress cracking resistance is better than HDPE. MDPE is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures.

LLDPE is defined by a density range of 0.915–0.925 g/cm^3. LLDPE is a substantially linear polymer with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). LLDPE has higher tensile strength than LDPE, 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. Cable covering, 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 2009 the world LLDPE market reached a volume of almost 24 billion US-dollars (17 billion Euro).

LDPE is defined by a density range of 0.910–0.940 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. LDPE is created by free radical polymerization. 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 2009 the global LDPE market had a volume of circa 22.2 billion US-dollars (15.9 billion Euro).

VLDPE is defined by a density range of 0.880–0.915 g/cm^3. VLDPE is a substantially linear polymer with high levels of short-chain branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). VLDPE is most commonly produced using metallocene catalysts due to the greater co-monomer incorporation exhibited by these catalysts. VLDPEs are used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap as well as impact modifiers when blended with other polymers.

Recently much research activity has focused on the nature and distribution of long chain branches in polyethylene. In HDPE a relatively small number of these branches, perhaps 1 in 100 or 1,000 branches per backbone carbon, can significantly affect the rheological properties of the polymer.

Ethylene copolymers

In addition to copolymerization with alpha-olefins, ethylene can also be copolymerized with a wide range of other monomers and ionic composition that creates ionized free radicals. Common examples include vinyl acetate (the resulting product is ethylene-vinyl acetate copolymer, or EVA, widely used in athletic-shoe sole foams) and a variety of acrylates (applications include packaging and sporting goods).

History

Polyethylene was first synthesized by the German chemist Hans von Pechmann who prepared it by accident in 1898 while heating diazomethane. When his colleagues Eugen Bamberger and Friedrich Tschirner characterized the white, waxy, substance that he had created they recognized that it contained long $-CH_2-$ chains and termed it *polymethylene*.

The first industrially practical polyethylene synthesis was discovered (again by accident) in 1933 by Eric Fawcett and Reginald Gibson at the ICI works in Northwich, England. Upon applying extremely high pressure (several hundred atmospheres) to a mixture of ethylene and benzaldehyde they again produced a white, waxy, material. Because the reaction had been initiated by trace oxygen contamination in their apparatus, the experiment was, at first, difficult to reproduce. It was not until 1935 that another ICI chemist, Michael Perrin, developed this accident into a reproducible high-pressure synthesis for polyethylene that became the basis for industrial LDPE production beginning in 1939. But because of World War Two commercial production was halted and secrecy imposed and the new ICI process was used to produce polyethylene for insulation of wires and cables in radar sets. During World War Two further research was done in the US on the ICI process and in 1944 Bakelite Corporation at Sabine, Texas and Du Pont at Charleston, West Virginia, began large scale commercial production under license from ICI.

Subsequent landmarks in polyethylene synthesis have revolved around the development of several types of catalyst that promote ethylene polymerization at more mild temperatures and pressures. The first of these was a chromium trioxide-based catalyst discovered in 1951 by Robert Banks and J. Paul Hogan at Phillips Petroleum. In 1953 the German chemist Karl Ziegler developed a catalytic system based on titanium halides and organoaluminium compounds that worked at even milder conditions than the Phillips catalyst. The Phillips catalyst is less expensive and easier to work with, however, and both methods are used in industrial practice.

By the end of the 1950s both the Phillips- and Ziegler-type catalysts were being used for HDPE production. Phillips initially had difficulties producing a HDPE product of uniform quality and filled warehouses with off-specification plastic. However, financial ruin was unexpectedly averted in 1957 when the hula hoop, a toy consisting of a circular polyethylene tube, became a fad among youth in the United States.

A third type of catalytic system, one based on metallocenes, was discovered in 1976 in Germany by Walter Kaminsky and Hansjörg Sinn. The Ziegler and metallocene catalyst families have since proven to be very flexible at copolymerizing ethylene with other olefins and have become the basis for the wide range of polyethylene resins available today, including very low density polyethylene and linear low-density polyethylene. Such resins, in the form of fibers like Dyneema, have (as of 2005) begun to replace aramids in many high-strength applications.

Until recently the metallocenes were the most active single-site catalysts for ethylene polymerisation known—new catalysts are typically compared to zirconocene dichloride. Much effort is currently being exerted on developing new, single-site (so-called post-metallocene) catalysts that may allow greater tuning of the polymer structure than is possible with metallocenes. Recently work by Fujita at the Mitsui corporation (amongst others) has demonstrated that certain salicylaldimine complexes of Group 4 metals show substantially higher activity than the metallocenes.

Physical properties

Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range 120 to 130 °C (248 to 266 °F). The melting point for average, commercial, low-density polyethylene is typically 105 to 115 °C (221 to 239 °F).

Most LDPE, MDPE and HDPE grades have excellent chemical resistance and do not dissolve at room temperature because of their crystallinity. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

When incinerated, polyethylene burns slowly with a blue flame having a yellow tip and gives off an odour of paraffin. The material continues burning on removal of the flame source and produces a drip.

Ecological problem

Although polyethylene can be recycled, most of the commercial polyethylene ends up in landfills, and in the oceans such as the Great Pacific Garbage Patch. Polyethylene is not considered biodegradable, because, except when it is exposed to UV from sunlight, it takes several centuries until it is efficiently degraded. In May 2008, Daniel Burd, a 16-year-old Canadian, won the Canada-Wide Science Fair in Ottawa after discovering that *Pseudomonas Fluorescens*, with the help of "Sphingomonas" two types of bacteria, can degrade over 40% of the weight of plastic bags in less than three months. Researchers are yet to find a practical application for this finding, however.

Bio-derived polyethylene

Braskem and Toyota Tsusho Corporation started Joint marketing activities for producing polyethylene from sugar cane. Braskem will build a new facility at their existing industrial unit in Triunfo, RS, Brazil with an annual production capacity of 200,000 short tons (180,000,000 kg), and will produce High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE) from bioethanol derived from sugarcane.

Polyethylene can also be made from other feedstocks, including wheat grain and sugar beet

Joining

Commonly used methods for joining include:

- Hot gas welding

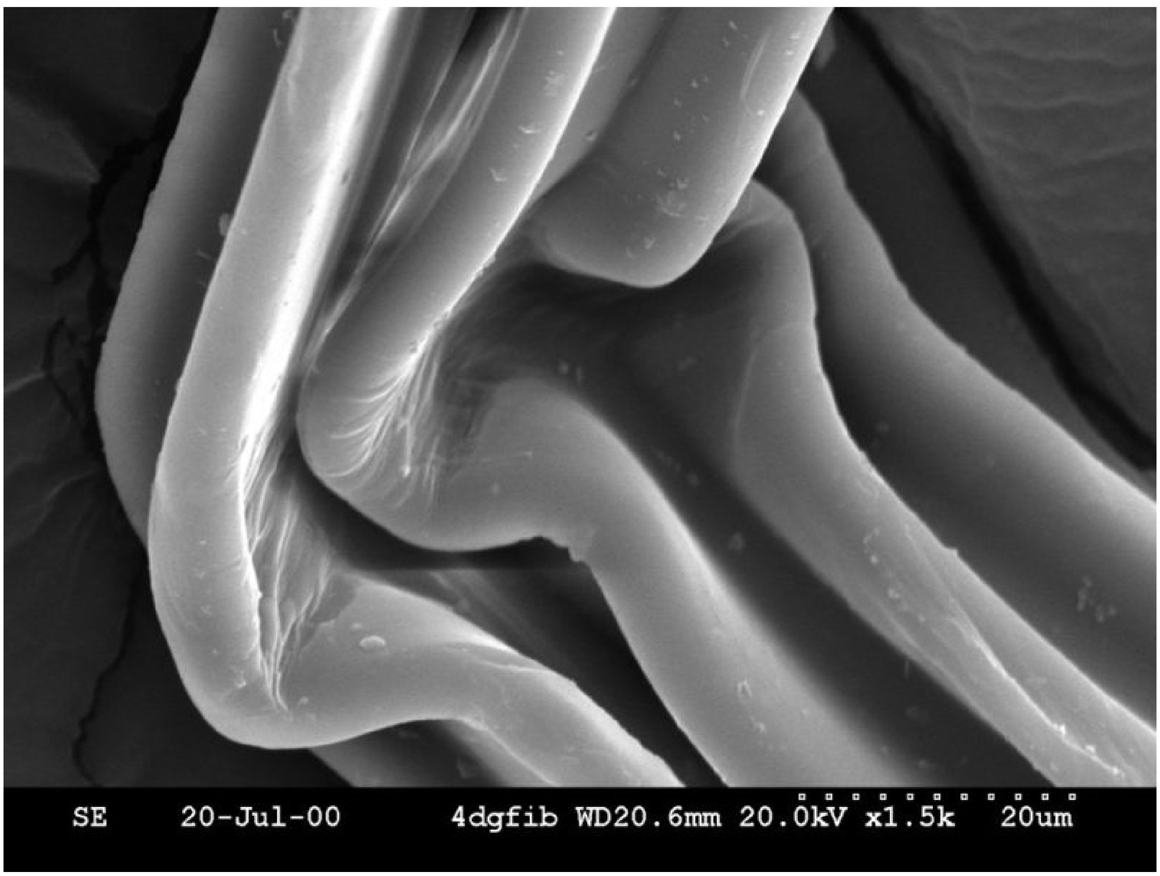
- Fastening
- Infrared welding
- Laser welding
- Ultrasonic welding

Adhesives and solvents are rarely used because polyethylene is nonpolar and has a high resistance to solvents. Pressure sensitive adhesives (PSA) are feasible if the surface is flame treated or corona treated. Commonly used adhesives include:

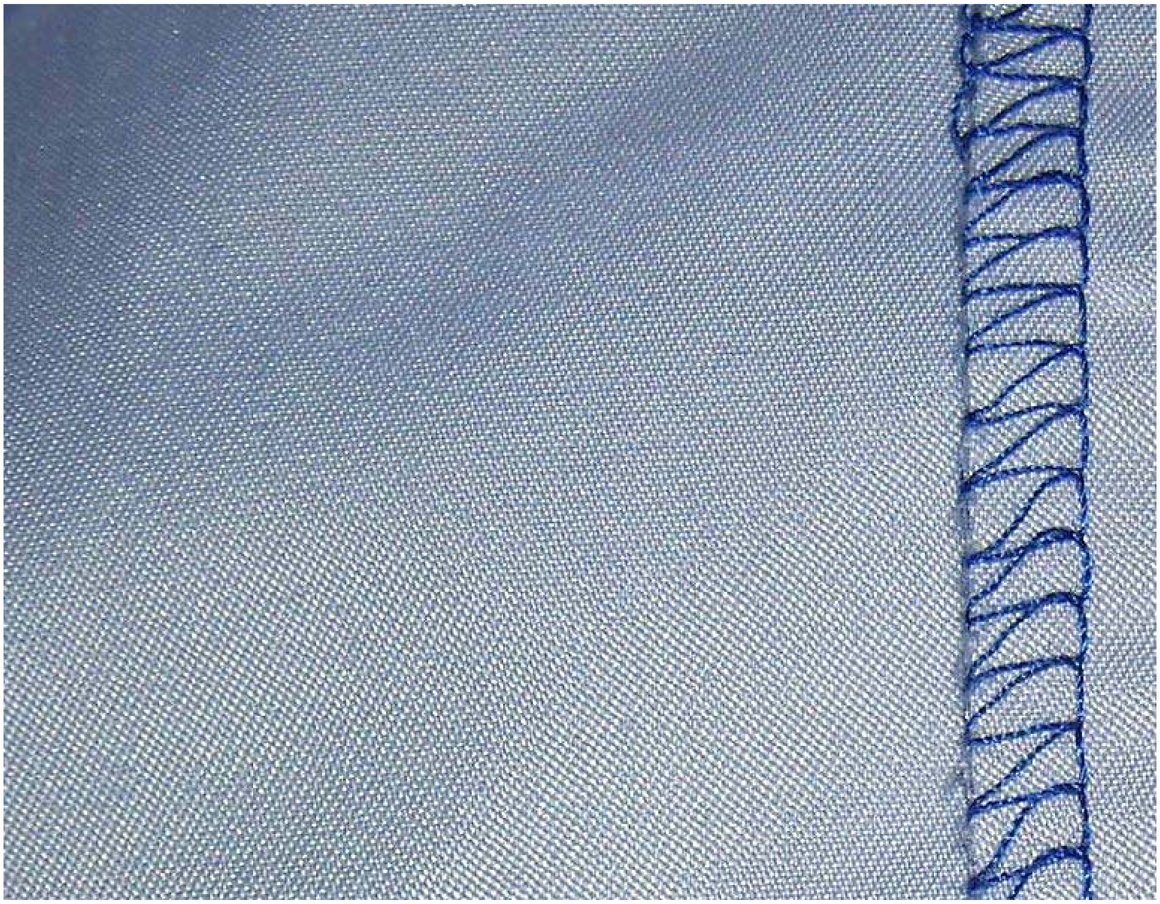
- Dispersion of solvent-type PSAs
- Polyurethane contact adhesives
- Two-part polyurethane or epoxy adhesives
- Vinyl acetate copolymer hot melt adhesives

Chapter- 7

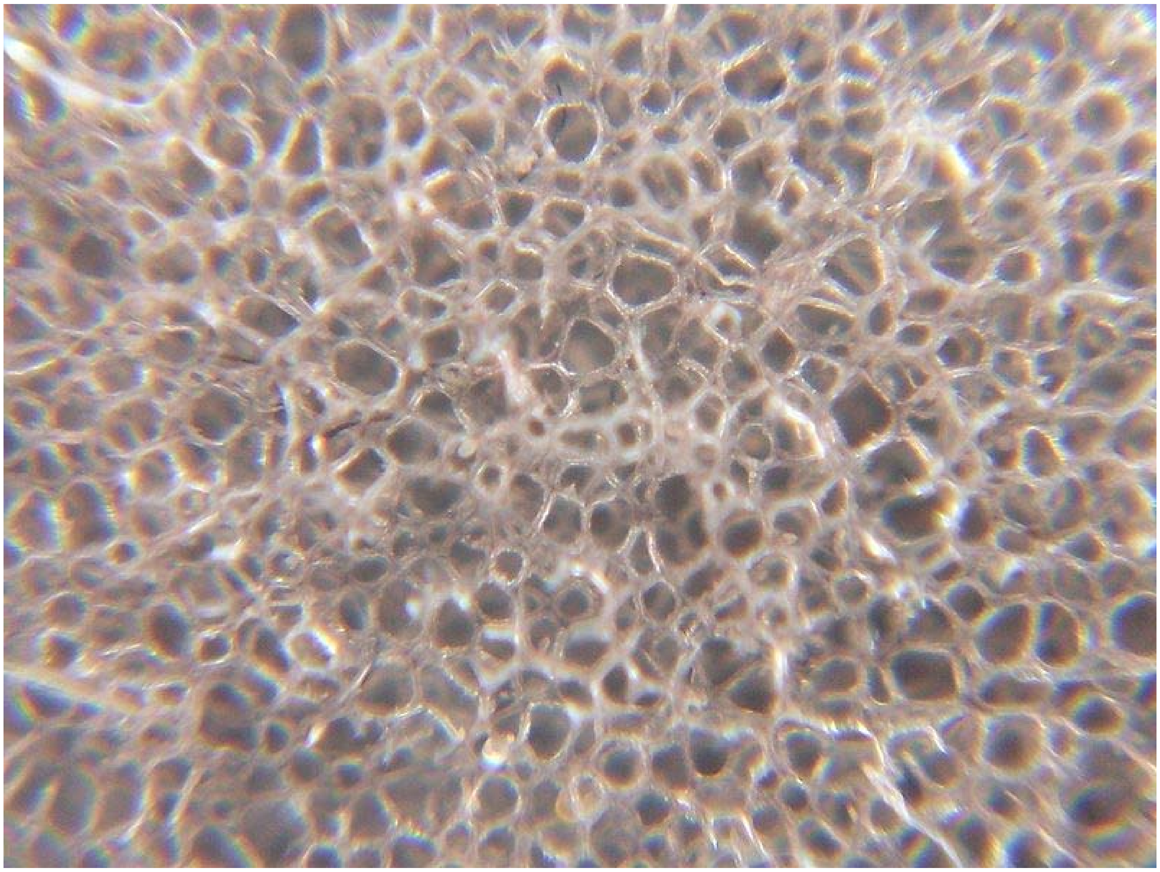
Polyester



SEM picture of a bend in a high-surface area polyester fiber with a seven-lobed cross section



Close-up of a polyester shirt



Supermacro closeup of a speaker cover fabric

Polyester is a category of polymers which contain the ester functional group in their main chain. Although there are many polyesters, the term "polyester" as a specific material most commonly refers to polyethylene terephthalate (PET). Polyesters include naturally-occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polycarbonate and polybutyrate. Natural polyesters and a few synthetic ones are biodegradable, but most synthetic polyesters are not.

Depending on the chemical structure polyester can be a thermoplastic or thermoset, however the most common polyesters are thermoplastics.

Fabrics woven from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets and upholstered furniture. Industrial polyester fibers, yarns and ropes are used in tyre 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.

While synthetic clothing in general is perceived by many as having a less-natural feel compared to fabrics woven from natural fibres (such as cotton and wool), polyester fabrics can provide specific advantages over natural fabrics, such as improved wrinkle resistance, durability and high color retention. As a result, polyester fibres are sometimes spun together with natural fibres to produce a cloth with blended properties. Synthetic fibres also can create materials with superior water, wind and environmental resistance compared to plant-derived fibres.

Polyesters are also used to make "plastic" bottles, films, tarpaulin, canoes, liquid crystal displays, holograms, filters, dielectric film for capacitors, film insulation for wire and insulating tapes.

Liquid crystalline polyesters are among the first industrially-used liquid crystal polymers. They are used for their mechanical properties and heat-resistance. These traits are also important in their application as an abradable seal in jet engines.

Polyesters are widely used as a finish on high-quality wood products such as guitars, pianos and vehicle/yacht interiors. Burns Guitars, Rolls Royce and Sunseeker are a few companies that use polyesters to finish their products. Thixotropic properties of spray-applicable polyesters make them ideal for use on open-grain timbers, as they can quickly fill wood grain, with a high-build film thickness per coat. Cured polyesters can be sanded and polished to a high-gloss, durable finish.

Types

Polyesters as thermoplastics may change shape after the application of heat. While combustible at high temperatures, polyesters tend to shrink away from flames and self-extinguish upon ignition. Polyester fibres have high tenacity and E-modulus as well as low water absorption and minimal shrinkage in comparison with other industrial fibres.

Unsaturated polyesters (UPR) are thermosetting resins. They are used as casting materials, fiberglass laminating resins and non-metallic auto-body fillers. Fibreglass-reinforced unsaturated polyesters find wide application in bodies of yachts and as body parts of cars.

According to the composition of their main chain, polyesters can be:

Composition of the main chain	Number of repeating units	Examples of polyesters	Examples of manufacturing methods
Aliphatic	Homopolymer	Polyglycolide or Polyglycolic acid (PGA)	Polycondensation of glycolic acid
		Polylactic acid (PLA)	Ring-opening polymerization of lactide
		Polycaprolactone (PCL)	Ring-opening polymerization of caprolactone
	Copolymer	Polyethylene adipate	

		(PEA)	
		Polyhydroxyalkanoate (PHA)	
Semi-aromatic	Copolymer	Polyethylene terephtalate (PET)	Polycondensation of terephthalic acid with ethylene glycol
		Polybutylene terephthalate (PBT)	Polycondensation of terephthalic acid with 2,3-butanediol
		Polytrimethylene terephthalate (PTT)	Polycondensation of terephthalic acid with 1,3-propanediol
		Polyethylene naphthalate (PEN)	Polycondensation of at least one naphthalene dicarboxylic acid with ethylene glycol
Aromatic	Copolymer	Vectran	Polycondensation of 4-hydroxybenzoic acid and 6-hydroxynaphthalene-2-carboxylic acid

Increasing the aromatic parts of polyesters increases their glass transition temperature, melting temperature, thermal stability, chemical stability...

Polyesters can also be telechelic oligomers like the polycaprolactone diol (PCL) and the polyethylene adipate diol (PEA). They are then used as prepolymers.

Industry

Basics

Polyester is a synthetic polymer made of purified terephthalic acid (PTA) or its dimethyl ester dimethyl terephthalate (DMT) and monoethylene glycol (MEG). With 18% market share of all plastic materials produced, it ranges third after polyethylene (33.5%) and polypropylene (19.5%).

The main raw materials are described as follows:

- **Purified terephthalic acid – PTA – CAS-No.: 100-21-0**

  Synonym: 1,4 benzenedicarboxylic acid,
  Sum formula; $C_6H_4(COOH)_2$, mol weight: 166.13

- **Dimethylterephthalate – DMT – CAS-No: 120-61-6**

  Synonym: 1,4 benzenedicarboxylic acid dimethyl ester

Sum formula $C_6H_4(COOCH_3)_2$, mol weight: 194.19

- **Mono Ethylene Glycol – MEG – CAS No.: 107-21-1**

  Synonym: 1,2 ethanediol
  Sum formula: $C_2H_6O_2$, mol weight: 62,07

To make a polymer of high molecular weight a catalyst is needed. The most common catalyst is antimony trioxide (or antimony tri acetate):

Antimony trioxide – ATO – CAS-No.: 1309-64-4 Molecular weight: 291.51 Sum formula: Sb_2O_3

In 2008, about 10,000 tonnes Sb_2O_3 were used to produce around 49 million tonnes polyethylene terephthalate.

Polyester is described as follows:

Polyethylene Terephthalate CAS-No.: 25038-59-9 Synonym/abbreviations: polyester, PET, PES Sum Formula: H-[$C_{10}H_8O_4$]-n=60–120 OH, molelcular unit weight: 192.17

There are several reasons for the importance of Polyester:

- The relatively easy accessible raw materials PTA or DMT and MEG
- The very well understood and described simple chemical process of polyester synthesis
- The low toxicity level of all raw materials and side products during polyester production and processing
- The possibility to produce PET in a closed loop at low emissions to the environment
- The outstanding mechanical and chemical properties of polyester
- The recyclability
- The wide variety of intermediate and final products made of polyester.

In table 1 the estimated world polyester production is shown. Main applications are textile polyester, bottle polyester resin, film polyester mainly for packaging and specialty polyesters for engineering plastics. According to this table, the world's total polyester production might exceed 50 million tons per annum before the year 2010.

Table 1: World polyester production

	Market size per year	
Product type	2002 [Million tonnes/year]	2008 [Million tonnes/year]
Textile-PET	20	39
Resin, bottle/A-PET	9	16

Film-PET	1.2	1.5
Special polyester	1	2.5
Total	31.2	49

Raw material producer

The raw materials PTA, DMT, and MEG are mainly produced by large chemical companies which are sometimes integrated down to the crude oil refinery where *p*-Xylene is the base material to produce PTA and liquefied petroleum gas (LPG) is the base material to produce MEG. Large PTA producers are for instance BP, Reliance, Sinopec, SK-Chemicals, Mitsui, and Eastman Chemicals. MEG production is in the hand of about 10 global players which are headed by MEGlobal a JV of DOW and PIC Kuweit followed by Sabic.

Polyester processing

After the first stage of polymer production in the melt phase, the product stream divides into two different application areas which are mainly textile applications and packaging applications. In figure 2 the main applications of textile and packaging polyester are listed.

Table 2: Textile and packaging polyester application list

Polyester-based polymer (melt or pellet)	
Textile	**Packaging**
Staple fiber (PSF)	Bottles for CSD, Water, Beer, Juice, Detergents
Filaments POY, DTY, FDY	A-PET Film
Technical yarn and tire cord	Thermoforming
Non-woven and spunbond	BO-PET Biaxial oriented Film
Mono-filament	Strapping

Abbreviations: PSF = Polyester Staple Fiber; POY = Partially Oriented Yarn; DTY = Draw Textured Yarn; FDY = Fully Drawn Yarn; CSD = Carbonated Soft Drink; A-PET = Amorphous Polyester Film; BO-PET = Biaxial Oriented Polyester Film;

A comparable small market segment (much less than 1 million tonnes/year) of polyester is used to produce engineering plastics and masterbatch.

In order to produce the polyester melt with a high efficiency, high-output processing steps like staple fiber (50–300 tonnes/day per spinning line) or POY /FDY (up to 600 tonnes/day split into about 10 spinning machines) are meanwhile more and more horizontal, integrated, direct processes. This means the polymer melt is directly converted into the textile fibers or filaments without the common step of pelletizing. We are talking about full horizontal integration when polyester is produced at one site starting from crude oil or distillation products in the chain oil → benzene → PX → PTA → PET melt → fiber/filament or bottle-grade resin. Such integrated processes are meanwhile established in more or less interrupted processes at one production site. Eastman Chemicals introduced at first the idea to close the chain from PX to PET resin with their so-called INTEGREX process. The capacity of such horizontal, integrated productions sites is >1000 tonnes/day and can easily reach 2500 tonnes/day.

Besides the above mentioned large processing units to produce staple fiber or yarns, there are ten thousands of small and very small processing plants, so that one can estimate that polyester is processed and recycled in more than 10 000 plants around the globe. This is without counting all the companies involved in the supply industry, beginning with engineering and processing machines and ending with special additives, stabilizers and colors. This is a gigantic industry complex and it is still growing by 4–8% per annum, depending on the world region. Useful information about the polyester industry can be found under where a “Who is Producing What in the Polyester Industry” is gradually being developed.

Synthesis

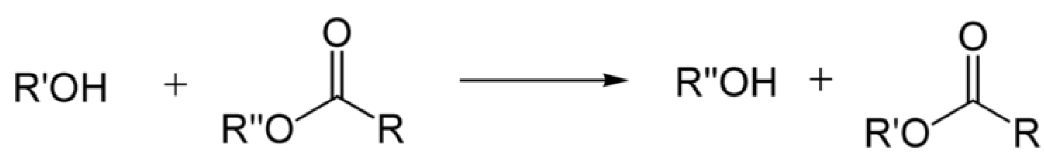
Synthesis of polyesters is generally achieved by a polycondensation reaction. The general equation for the reaction of a diol with a diacid is:

$$(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \rightarrow HO[ROOCR'COO]_nROH + 2n\ H_2O$$

Azeotrope esterification

In this classical method, an alcohol and a carboxylic acid react to form a carboxylic ester. To assemble a polymer, the water formed by the reaction must be continually removed by azeotrope distillation.

Alcoholic transesterification



Transesterification: An alcohol-terminated oligomer and an ester-terminated oligomer condense to form an ester linkage, with loss of an alcohol. R and R' are the two oligomer chains, R'' is a sacrificial unit such as a methyl group (methanol is the byproduct of the esterification reaction).

Acylation (HCl method)

The acid begins as an acid chloride, and thus the polycondensation proceeds with emission of hydrochloric acid (HCl) instead of water. This method can be carried out in solution or as an enamel.

Silyl method
In this variant of the HCl method, the carboxylic acid chloride is converted with the trimethyl silyl ether of the alcohol component and production of trimethyl silyl chloride is obtained

Acetate method (esterification)

Silyl acetate method

Ring-opening polymerization

Aliphatic polyesters can be assembled from lactones under very mild conditions, catalyzed anionically, cationically or metallorganically.

Cross-linking

Unsaturated polyesters are thermosetting resins. They are generally copolymers prepared by polymerizing one or more diol with saturated and unsaturated dicarboxylic acids (maleic acid, fumaric acid...) or their anhydrides. The double bond of unsaturated polyesters reacts with a vinyl monomer mainly the styrene, resulting in a 3-D cross-linked structure. This structure acts as a thermoset. The cross-linking is initiated through an exothermic reaction involving an organic peroxide, such as methyl ethyl ketone peroxide or benzoyl peroxide.

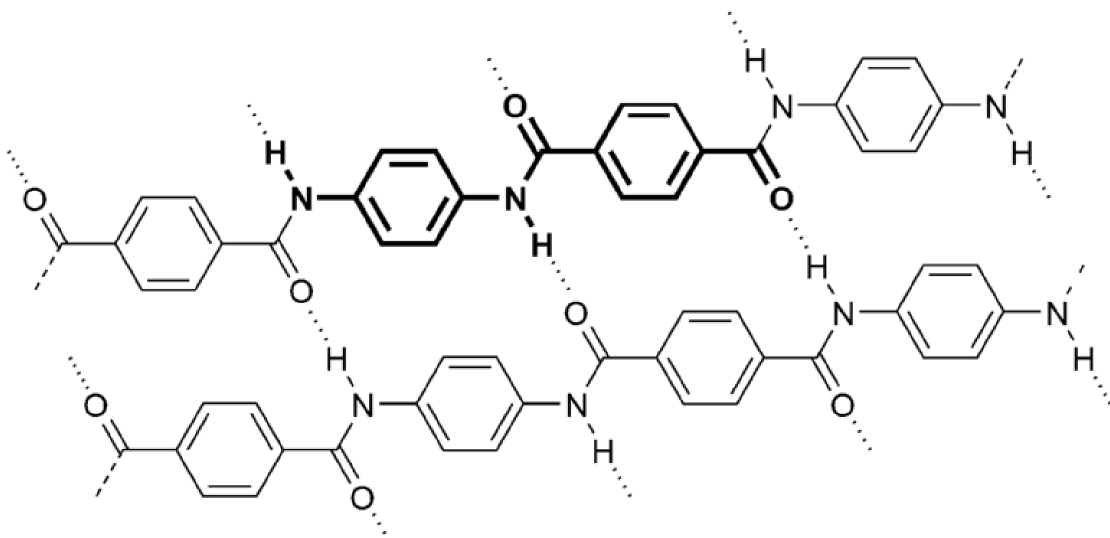
Health effects

A study published in 1993 found that polyester underwear reduced sperm count and sperm motility in male dogs. Similar studies have shown similar results in humans and rats. The cause is not known but is believed to be due to an electrostatic field created by the fabric.

Chapter- 8

Aramid and Zylon

Aramid



Para-aramid structure

Aramid fibers are a class of heat-resistant and strong synthetic fibers. They are used in aerospace and military applications, for ballistic rated body armor fabric and ballistic composites, in bicycle tires, and as an asbestos substitute. The name is a portmanteau of "aromatic polyamide". They are fibers in which the chain molecules are highly oriented along the fiber axis, so the strength of the chemical bond can be exploited.

History

Aromatic polyamides were first introduced in commercial applications in the early 1960s, with a meta-aramid fiber produced by DuPont under the tradename Nomex. This fiber, which handles similarly to normal textile apparel fibers, is characterized by its excellent resistance to heat, as it neither melts nor ignites in normal levels of oxygen. It is used extensively in the production of protective apparel, air filtration, thermal and electrical insulation as well as a substitute for asbestos. Meta-aramid is also produced in the Netherlands and Japan by Teijin under the tradename Teijinconex, in China by Yantai under the tradename New Star and also by SRO Group (China) under the trade name X-Fiper, a variant of meta-aramid in France by Kermel under the tradename Kermel.

Based on earlier research by Monsanto Company and Bayer, a fiber - para-aramid - with much higher tenacity and elastic modulus was also developed in the 1960s-1970s by DuPont and Akzo Nobel, both profiting from their knowledge of rayon, polyester and nylon processing.

Much work was done by Stephanie Kwolek in 1961 while working at DuPont, and that company was the first to introduce a *para-aramid* called Kevlar in 1973. A similar fiber called Twaron with roughly the same chemical structure was introduced by Akzo in 1978. Due to earlier patents on the production process, Akzo and DuPont had a patent war in the 1980s. Twaron is currently owned by the Teijin company.

Para-aramids are used in many high-tech applications, such as aerospace and military applications, for "bullet-proof" body armor fabric.

The Federal Trade Commission definition for aramid fiber is:

A manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages, (-CO-NH-) are attached directly to two aromatic rings.

Production

World capacity of para-aramid production is estimated at about 41,000 tons/yr in 2002 and increases each year by 5-10%. In 2007 this means a total production capacity of around 55,000 tons/yr.

Polymer preparation

Aramids are generally prepared by the reaction between an amine group and a carboxylic acid halide group. Simple AB homopolymers may look like:

$$n\mathrm{NH_2\text{-}Ar\text{-}COCl} \rightarrow \mathrm{\text{-}(NH\text{-}Ar\text{-}CO)_n\text{-}} + n\mathrm{HCl}$$

The most well-known aramids (Kevlar, Twaron, Nomex, New Star, Teijinconex and X-fiper) are AABB polymers. Nomex, Teijinconex, New Star and X-Fiper contain predominantly the meta-linkage and are poly-*metaphenylene isophtalamide*s (MPIA). Kevlar and Twaron are both *p*-phenylene terephtalamides (PPTA), the simplest form of the AABB para-polyaramide. PPTA is a product of *p*-phenylene diamine (PPD) and terephtaloyl dichloride (TDC or TCl). Production of PPTA relies on a co-solvent with an ionic component (calcium chloride ($CaCl_2$)) to occupy the hydrogen bonds of the amide groups, and an organic component (N-methyl pyrrolidone (NMP)) to dissolve the aromatic polymer. Prior to the invention of this process by Leo Vollbracht, who worked at the Dutch chemical firm Akzo, no practical means of dissolving the polymer was known. The use of this system led to a patent war between Akzo and DuPont.

Spinning

After production of the polymer, the aramid fiber is produced by spinning the solved polymer to a solid fiber from a liquid chemical blend. Polymer solvent for spinning PPTA is generally 100% anhydrous sulfuric acid (H_2SO_4).

Appearances

- Fiber
- Chopped fiber
- Powder
- Pulp

Other types of aramids

Besides meta-aramids like Nomex, other variations belong to the aramid fiber range. These are mainly of the **copolyamide** type, best known under the brand name Technora, as developed by Teijin and introduced in 1976. The manufacturing process of Technora reacts PPD and 3,4'-diaminodiphenylether (3,4'-ODA) with terephtaloyl chloride (TCl). This relatively simple process uses only one amide solvent and therefore spinning can be done directly after the polymer production.

Aramid fiber characteristics

Aramids share a high degree of orientation with other fibers such as ultra high molecular weight polyethylene, a characteristic which dominates their properties.

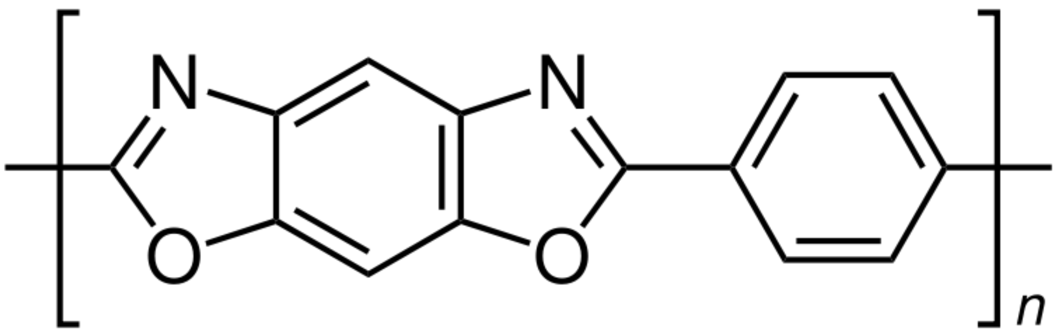
General

- good resistance to abrasion
- good resistance to organic solvents
- nonconductive
- no melting point, degradation starts from 500°C
- low flammability
- good fabric integrity at elevated temperatures
- sensitive to acids and salts
- sensitive to ultraviolet radiation
- prone to static build-up unless finished

Para-aramids

- para-aramid fibers such as Kevlar and Twaron, provide outstanding strength-to-weight properties
- high Young's modulus
- high tenacity
- low creep
- low elongation at break (~3.5%)
- difficult to dye - usually solution dyed

Zylon



The structure of Zylon

Zylon (IUPAC name: **poly(*p*-phenylene-2,6-benzobisoxazole)**) is a trademarked name for a range of thermoset liquid crystalline polyoxazole. This synthetic polymer material is manufactured by the Toyobo Corporation. Zylon was invented and developed by SRI International in the 1980s. Like Kevlar, Zylon is used in a number of applications that require very high strength with excellent thermal stability. Tennis racquets, table tennis blades, various medical applications, and some of the Martian rovers are some of the more well known instances. More common usage is in drive belts for snow mobiles manufactured by MBL USA Corporation.

Usage

Body armor

Zylon gained wide use in U.S. police officers body armor protection in 1998 with its introduction by Second Chance Body Armor, Inc. But protective vests constructed with Zylon became controversial in late 2003 when Oceanside, CA Police Officer Tony Zeppetella's and Forest Hills, PA Police Officer Ed Limbacher's vests failed, leaving

Zeppetella mortally wounded and Limbacher seriously injured. Some studies subsequently reported that the Zylon vests may degrade rapidly, leaving wearers with significantly less protection than expected. Second Chance eventually recalled all of its zylon-containing vests, which led to its subsequent bankruptcy. In early 2005, Armor Holdings, Inc. first recalled its existing Zylon-based products, and decreased the rated lifespan warranty of new vests from 60 months to 30 months. In August 2005, AHI decided to discontinue manufacturing all of its Zylon-containing vests. This was largely based on the actions of the U.S. government's National Institute of Justice, which decertified Zylon for use in its approved models of ballistic vests for law enforcement.

Space elevator research

A competition was held in the Wirefly X Prize Cup in Las Cruces, New Mexico, US, on October 20–21, 2006. A team from the University of British Columbia entered into the Tether Challenge, using a construction made from Zylon fibers. The house tether used by Spaceward that the other teams would have to beat in strength by 50% in the 2007 strong tether challenge, was made of Zylon.

Formula One racing

As has been the case since 2001, Zylon tethers are used in Formula One to affix the wheel to the chassis thus preventing the wheel from ejecting in to a crowded area in the event of an accident which causes the wheel to become airborne. Starting in the 2007 season, the driver's cockpit must now be clad in special anti-penetration panels made of Zylon. The Indy Racing League began using Zylon in 2008.

Standing rigging

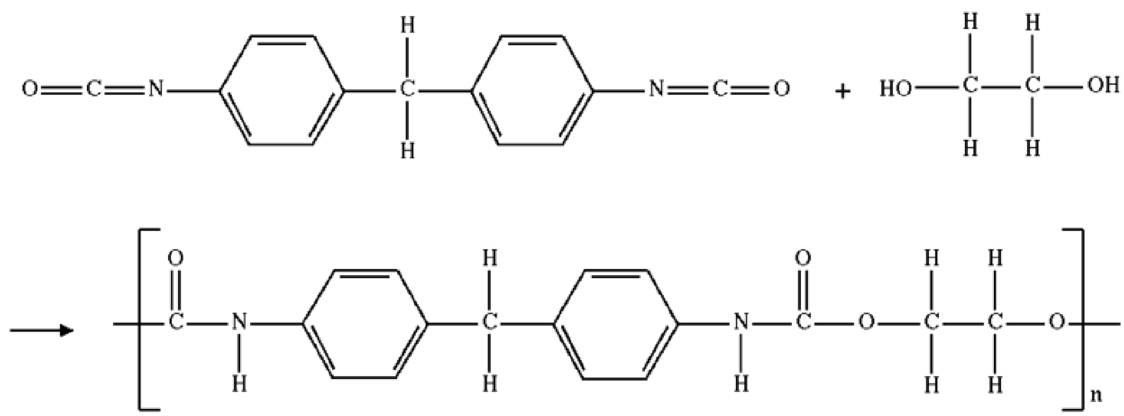
On modern racing yachts Zylon is used for parts of the standing rigging. It is used as shrouds and stays, except the forestay due to torsion weakening the fiber. The PBO fiber degrade by UV and visible light, seawater and chafing and is therefore protected by a synthetic melted-on jacket. These ropes are manufactured by Linear Composites LTD and Applied Fiber / Powerlite rigging in the US. It is claimed to be 65% lighter than traditional rigging at 110–130% of the price of rodrigging. Based on laboratory tests, superior durability is also claimed. Zylon has a high Young's modulus of 270GPa, meaning that it is very stiff.

Conductive textile

Zylon has been incorporated as the base fiber for AmberStrand-Z series conductive fibers made by Syscom Advanced Materials, Inc. Currently offered in three different tow or strand sizes, the Zylon fiber is plated with nickel, copper, silver, or gold. The conductive fiber is used for electronic textiles, EMI shielding in woven or knit sheets, or as a braid over wires, and for signal transmission or current conduction. This conductive fiber combines the advantages of Zylon (strength, high temperature, durability, light weight, etc.) with the electrical properties of various metals. The conductive yarns can be sewn, braided, knit, or simply insulated like a bare wire.

Chapter- 9

Polyurethane



Example of synthesis of a polyurethane. Note the urethane groups -NH-(C=O)-O- linking the units of the product.

A **polyurethane** (IUPAC abbreviation **PUR**, but commonly abbreviated **PU**) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization (also known as polyaddition) by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst.

Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments).

Polyurethane products are often called "urethanes". They should not be confused with the specific substance urethane, also known as ethyl carbamate. Polyurethanes are neither produced from ethyl carbamate, nor do they contain it.

History

The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters. Initially, work focused on the production of fibres and flexible foams. With development constrained by World War II (when PUs were applied on a limited scale as aircraft coating), it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called *imitation swiss cheese* by the inventors) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibers were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO).

The first commercially available polyether polyol, poly(tetramethylene ether) glycol, was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. Less expensive polyalkylene glycols were introduced by BASF and Dow Chemical in 1957. Polyether polyols offered technical and commercial advantages such as low cost, ease of handling, and better hydrolytic stability over polyester polyols and quickly replaced them in the manufacture of polyurethane goods. Other PU pioneers were Union Carbide and Mobay, a U.S. Monsanto/Bayer joint venture. In 1960 more than 45,000 metric tons of flexible polyurethane foams were produced. As the decade progressed, the availability of chlorofluoroalkane blowing agents, inexpensive polyether polyols, and methylene diphenyl diisocyanate (MDI) heralded the development and use of polyurethane rigid foams as high performance insulation materials. Rigid foams based on polymeric MDI (PMDI) offered better thermal stability and combustion characteristics than those based on TDI. In 1967, urethane modified polyisocyanurate rigid foams were introduced, offering even better thermal stability and flammability resistance compared to low-density insulation products. During the 1960s, automotive interior safety components such as instrument and door panels were produced by back-filling thermoplastic skins with semi-rigid foam.

In 1969, Bayer exhibited an all plastic car in Düsseldorf, Germany. Parts of this car were manufactured using a new process called RIM, Reaction Injection Molding. RIM technology uses high pressure impingement of liquid reactive components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes. Using diamine chain extenders and trimerization technology gave poly(urethane urea), poly(urethane isocyanurate), and polyurea RIM. The addition of fillers, such as milled glass, mica, and processed mineral fibres gave rise to reinforced RIM (RRIM), which provided improvements in flexural modulus (stiffness), reduction in coefficent of thermal expansion and thermal stability. This technology allowed production of the first plastic-body automobile in the United States, the Pontiac Fiero, in 1983. Further increases in flexural modulus were obtained by incorporating preplaced glass mats into the RIM mold cavity, also known broadly as resin injection molding (a process technology that also includes thermosetting polyester resins, epoxide resins, etc.) or more specifically for PUR systems as SRIM, or structural RIM.

Starting in the early 1980s, water-blown microcellular flexible foams were used to mold gaskets for panel and radial seal air filters in the automotive industry. Since then, increasing energy prices and the pressures to eliminate PVC plastisol from automotive applications have greatly increased market share. Costlier raw materials are offset by a significant decrease in part weight and in some cases, the elimination of metal end caps and filter housings. Highly filled polyurethane elastomers, and more recently unfilled polyurethane foams are now used in high temperature oil filter applications.

Polyurethane foam (including foam rubber) is often made by adding small amounts of volatile materials, so-called blowing agents, to the reaction mixture. These volatile chemicals yield important performance characteristics, primarily density reduction, cushioning/energy absorption and thermal insulation. In the early 1990s, because of their impact on ozone depletion, the Montreal Protocol led to the greatly reduced use of many chlorine-containing blowing agents, such as trichlorofluoromethane (CFC-11). Other haloalkanes, such as the hydrochlorofluorocarbon 1,1-dichloro-1-fluoroethane (HCFC-141b), were used as interim replacements until their phase out under the IPPC directive on greenhouse gases in 1994 and by the Volatile Organic Compounds (VOC) directive of the EU in 1997. By the late 1990s, the use of blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) became more widespread in North America and the EU, although chlorinated blowing agents remained in use in many developing countries.

Building on existing polyurethane spray coating technology and polyetheramine chemistry, extensive development of two-component polyurea spray elastomers took place in the 1990s. Their fast reactivity and relative insensitivity to moisture make them useful coatings for large surface area projects, such as secondary containment, manhole and tunnel coatings, and tank liners. Excellent adhesion to concrete and steel is obtained with the proper surface treatment and primer. During the same period, new two-component polyurethane and hybrid polyurethane-polyurea elastomer technology was used to enter the marketplace of spray-in-place load bed liners and military marine applications for the U.S. Navy. Even a one-part polyurethane is specified as high durability deck coatings under MIL-PRF-32171 for the US Navy. This technique for coating creates a durable, abrasion resistant composite with the metal substrate, and eliminates corrosion and brittleness associated with drop-in thermoplastic bed liners.

The potential for polyols derived from vegetable oils to replace petrochemical-based polyols began garnering attention beginning around 2004, partly due to the rising costs of petrochemical feedstocks and partially due to an enhanced public desire for environmentally friendly green products. One of the most vocal supporters of these polyurethanes made using natural oil polyols is the Ford Motor Company.

Chemistry

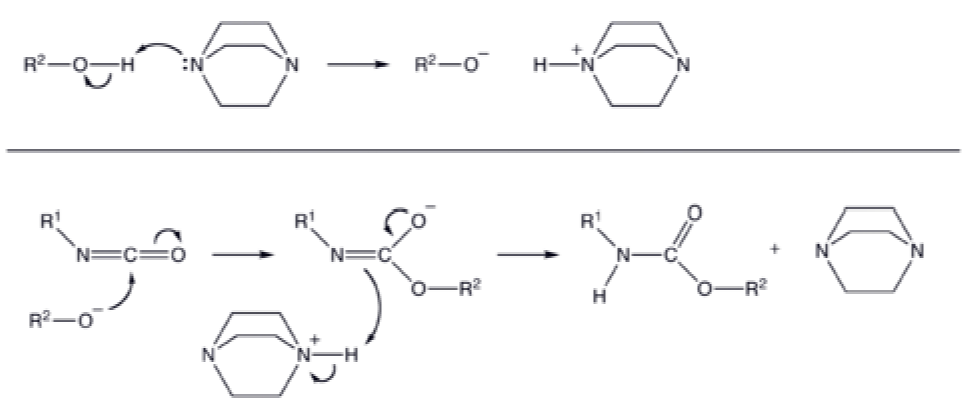
generalized polyurethane reaction
$R^1\text{-}N{=}C{=}O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{\underset{}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$

Polyurethanes are in the class of compounds called **reaction polymers**, which include epoxies, unsaturated polyesters, and phenolics. A urethane linkage is produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. In this case, a polyisocyanate is a molecule with two or more isocyanate functional groups, R-$(N{=}C{=}O)_{n \geq 2}$ and a polyol is a molecule with two or more hydroxyl functional groups, R'-$(OH)_{n \geq 2}$. The reaction product is a polymer containing the urethane linkage, -RNHCOOR'-. Isocyanates will react with any molecule that contains an active hydrogen. Importantly, isocyanates react with water to form a urea linkage and carbon dioxide gas; they also react with polyetheramines to form polyureas. Commercially, polyurethanes are produced by reacting a liquid isocyanate with a liquid blend of polyols, catalyst, and other additives. These two components are referred to as a polyurethane system, or simply a system. The isocyanate is commonly referred to in North America as the 'A-side' or just the 'iso'. The blend of polyols and other additives is commonly referred to as the 'B-side' or as the 'poly'. This mixture might also be called a 'resin' or 'resin blend'. In Europe the meanings for 'A-side' and 'B-side' are reversed. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers.

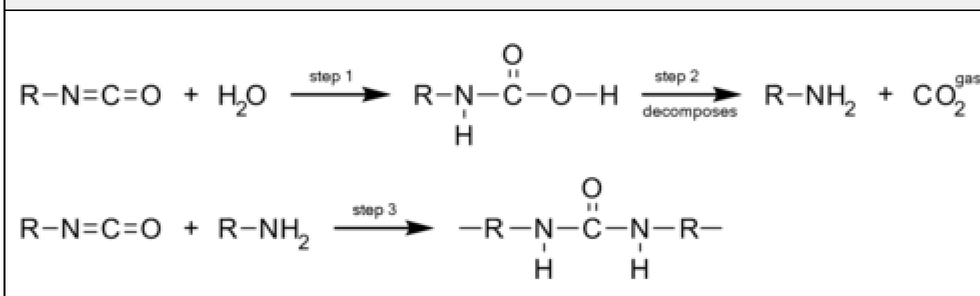
The first essential component of a polyurethane polymer is the isocyanate. Molecules that contain two isocyanate groups are called diisocyanates. These molecules are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates that contain three or more isocyanate functional groups. Isocyanates can be classed as aromatic, such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI); or aliphatic, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). An example of a polymeric isocyanate is polymeric diphenylmethane diisocyanate, which is a blend of molecules with two-, three-, and four- or more isocyanate groups, with an average functionality of 2.7. Isocyanates can be further modified by partially reacting them with a polyol to form a prepolymer. A quasi-prepolymer is formed when the stoichiometric ratio of isocyanate to hydroxyl groups is greater than 2:1. A true prepolymer is formed when the stoichiometric ratio is equal to 2:1. Important characteristics of isocyanates are their molecular backbone, % NCO content, functionality, and viscosity.

The second essential component of a polyurethane polymer is the polyol. Molecules that contain two hydroxyl groups are called diols, those with three hydroxyl groups are called triols, et cetera. In practice, polyols are distinguished from short chain or low-molecular weight glycol chain extenders and cross linkers such as ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DEG), glycerine, and trimethylolpropane (TMP). Polyols are polymers in their own right. They are formed by base-catalyzed addition of propylene oxide (PO), ethylene oxide (EO) onto a hydroxyl or amine containing initiator, or by polyesterification of a di-acid, such as adipic acid, with glycols, such as ethylene glycol or dipropylene glycol (DPG). Polyols extended with PO or EO are polyether polyols. Polyols formed by polyesterification are polyester polyols. The choice of initiator, extender, and molecular weight of the polyol greatly affect its physical state, and the physical properties of the polyurethane polymer. Important characteristics of polyols are their molecular backbone, initiator, molecular weight, % primary hydroxyl groups, functionality, and viscosity.

PU reaction mechanism catalyzed by a tertiary amine



carbon dioxide gas formed by reacting water and isocyanate



The polymerization reaction is catalyzed by tertiary amines, such as dimethylcyclohexylamine, and organometallic compounds, such as dibutyltin dilaurate or bismuth octanoate. Furthermore, catalysts can be chosen based on whether they favor the urethane (gel) reaction, such as 1,4-diazabicyclo[2.2.2]octane (also called DABCO or TEDA), or the urea (blow) reaction, such as bis-(2-dimethylaminoethyl)ether, or specifically drive the isocyanate trimerization reaction, such as potassium octoate.

One of the most desirable attributes of polyurethanes is their ability to be turned into foam. Blowing agents such as water, certain halocarbons such as HFC-245fa (1,1,1,3,3-pentafluoropropane) and HFC-134a (1,1,1,2-tetrafluoroethane), and hydrocarbons such as n-pentane, can be incorporated into the poly side or added as an auxiliary stream. Water reacts with the isocyanate to create carbon dioxide gas, which fills and expands cells created during the mixing process. The reaction is a three step process. A water molecule reacts with an isocyanate group to form a carbamic acid. Carbamic acids are unstable, and decompose forming carbon dioxide and an amine. The amine reacts with more isocyanate to give a substituted urea. Water has a very low molecular weight, so even though the weight percent of water may be small, the molar proportion of water may be high and considerable amounts of urea produced. The urea is not very soluble in the reaction mixture and tends to form separate "hard segment" phases consisting mostly of polyurea. The concentration and organization of these polyurea phases can have a significant impact on the properties of the polyurethane foam. Halocarbons and hydrocarbons are chosen such that they have boiling points at or near room temperature. Since the polymerization reaction is exothermic, these blowing agents volatilize into a gas during the reaction process. They fill and expand the cellular polymer matrix, creating a foam. It is important to know that the blowing gas does not create the cells of a foam. Rather, foam cells are a result of blowing gas diffusing into bubbles that are nucleated or stirred into the system at the time of mixing. In fact, high-density microcellular foams can be formed without the addition of blowing agents by mechanically frothing or nucleating the polyol component prior to use.

Surfactants are used to modify the characteristics of the polymer during the foaming process. They are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and surface defects. Rigid foam surfactants are designed to produce very fine cells and a very high closed cell content. Flexible foam surfactants are designed to stabilize the reaction mass while at the same time maximizing open cell content to prevent the foam from shrinking. The need for surfactant can be affected by choice of isocyanate, polyol, component compatibility, system reactivity, process conditions and equipment, tooling, part shape, and shot weight.

Though the properties of the polyurethane are determined mainly by the choice of polyol, the diisocyanate exerts some influence, and must be suited to the application. The cure rate is influenced by the functional group reactivity and the number of functional isocyanate groups. The mechanical properties are influenced by the functionality and the molecular shape. The choice of diisocyanate also affects the stability of the polyurethane upon exposure to light. Polyurethanes made with aromatic diisocyanates yellow with exposure to light, whereas those made with aliphatic diisocyanates are stable.

Softer, elastic, and more flexible polyurethanes result when linear difunctional polyethylene glycol segments, commonly called polyether polyols, are used to create the urethane links. This strategy is used to make spandex elastomeric fibers and soft rubber parts, as well as foam rubber. More rigid products result if polyfunctional polyols are used, as these create a three-dimensional cross-linked structure which, again, can be in the form of a low-density foam.

An even more rigid foam can be made with the use of specialty trimerization catalysts which create cyclic structures within the foam matrix, giving a harder, more thermally stable structure, designated as polyisocyanurate foams. Such properties are desired in rigid foam products used in the construction sector.

Careful control of viscoelastic properties — by modifying the catalysts and polyols used —can lead to memory foam, which is much softer at skin temperature than at room temperature.

There are then two main foam variants: one in which most of the foam bubbles (cells) remain closed, and the gas(es) remains trapped, the other being systems which have mostly open cells, resulting after a critical stage in the foam-making process (if cells did not form, or became open too soon, foam would not be created). This is a vitally important process: if the flexible foams have closed cells, their softness is severely compromised, they become pneumatic in feel, rather than soft; so, generally speaking, flexible foams are required to be open-celled.

The opposite is the case with most rigid foams. Here, retention of the cell gas is desired since this gas (especially the fluorocarbons referred to above) gives the foams their key characteristic: high thermal insulation performance.

A third foam variant, called microcellular foam, yields the tough elastomeric materials typically experienced in the coverings of car steering wheels and other interior automotive components.

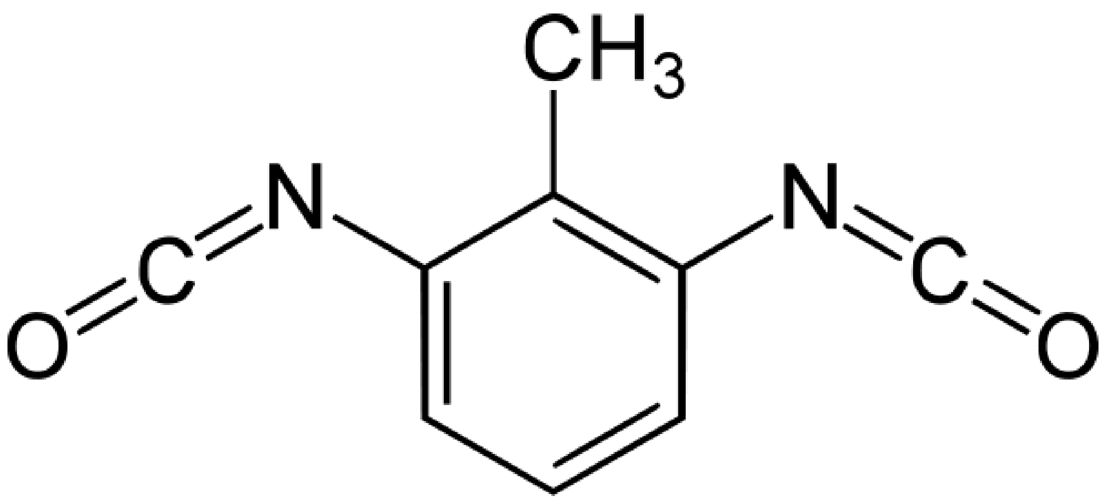
Raw materials

For the manufacture of polyurethane polymers, two groups of at least bifunctional substances are needed as reactants; compounds with isocyanate groups, and compounds with active hydrogen atoms. The physical and chemical character, structure, and molecular size of these compounds influence the polymerization reaction, as well as ease of processing and final physical properties of the finished polyurethane. In addition, additive such as catalysts, surfactants, blowing agents, cross linkers, flame retardants, light stabilizers, and fillers are used to control and modify the reaction process and performance characteristics of the polymer.

Isocyanates

Isocyanates with two or more functional groups are required for the formation of polyurethane polymers. Volume wise, aromatic isocyanates account for the vast majority of global diisocyanate production. Aliphatic and cycloaliphatic isocyanates are also important building blocks for polyurethane materials, but in much smaller volumes. There are a number of reasons for this. First, the aromatically linked isocyanate group is much more reactive than the aliphatic one. Second, aromatic isocyanates are more economical to use. Aliphatic isocyanates are used only if special properties are required for the final product. For example, light stable coatings and elastomers can only be obtained with aliphatic isocyanates. Even within the same class of isocyanates, there is a significant difference in reactivity of the functional groups based on steric hindrance. In the case of 2,4-toluene diisocyanate, the isocyanate group in the para position to the methyl group is much more reactive than the isocyanate group in the ortho position.

Phosgenation of corresponding amines is the main technical process for the manufacture of isocyanates. The amine raw materials are generally manufactured by the hydrogenation of corresponding nitro compounds. For example, toluenediamine (TDA) is manufactured from dinitrotoluene, which then converted to toluene diisocyanate (TDI). Diamino diphenylmethane or methylenedianiline (MDA) is manufactured from nitrobenzene via aniline, which is then converted to diphenylmethane diisocyanate (MDI).



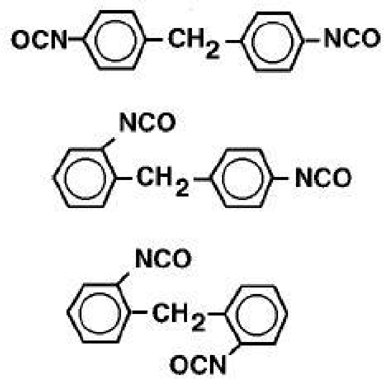
2,6-Diisocyanatotoluene

The two most important commercial, aromatic isocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). TDI consists of a mixture of the 2,4- and 2,6-diisocyanatotoluene isomers. The most important product is TDI-80 (TD-80), consisting of 80% of the 2,4-isomer and 20% of the 2,6-isomer. This blend is used extensively in the manufacture of polyurethane flexible slabstock and molded foam. TDI, and especially crude TDI and TDI/MDI blends can be used in rigid foam applications, but have been supplanted by polymeric MDI. TDI-polyether and TDI-polyester prepolymers are used in high performance coating and elastomer applications. Prepolymers are available that have been vacuum stripped of TDI monomer, which greatly reduces their toxicity. Diphenylmethane diisocyanate (MDI) has three isomers, 4,4'-MDI, 2,4'-MDI, and 2,2'-MDI, and is also polymerized to provide oligomers of functionality three and higher.

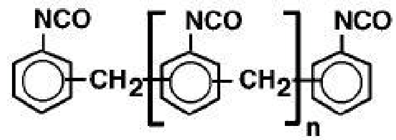
4,4'

2,4'

2,2'



Pure MDI's



Polymeric MDI's

Only the 4,4'-MDI monomer is sold commercially as a single isomer. It is provided either as a frozen solid or flake, or in molten form, and is used to manufacture high performance prepolymers. Monomer blends, consisting of approximately 50% of the 4,4'-isomer and 50% of the 2,4'-isomer, are liquid at room temperature and are used to manufacture prepolymers for polyurea spray elastomer applications. 4,4'-MDI blends containing MDI uretonimine, carbodiimide, and allophonate moieties are also liquid at room temperature, and are used in the manufacture of integral skin and microcellular foams. 4,4'-MDI-glycol prepolymers offer increased mechanical properties in the same applications, but are prone to freezing at temperatures below 20 °C. Polymeric MDI (PMDI) is used in rigid pour-in-place, spray foam, and molded foam applications. Polymeric MDI that contains a very high portion of high-functionality oligomers is used to manufacture polyurethane and polyisocyanurate rigid insulation boardstock. Modified PMDI, which contains high levels of MDI monomer, is used in the production of polyurethane flexible molded and microcellular foams. The relative percentage of the 4,4'- and 2,4'- isomers is adjusted to change the reactivity and storage stability of the isocyanate blend, as well as the firmness and other physical properties of the finished goods. Other aromatic isocyanate include p-phenylene diisocyanate (PPDI), naphthalene diisocyanate (NDI), and o-tolidine diisocyanate (TODI).

The most important aliphatic and cycloaliphatic isocyanates are 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate, IPDI), and 4,4'-diisocyanato dicyclohexylmethane (H_{12}MDI or hydrogenated MDI). They are used to produce light stable, non-yellowing polyurethane coatings and elastomers. Because of their volatility and toxicity, aliphatic isocyanate monomers are converted into prepolymers, biurets, dimers, and trimers for commercial use. HDI adducts are used extensively for weather and abrasion resistant coatings and lacquers. IPDI is used in the manufacture of coatings, elastomeric adhesives and sealants. H_{12}MDI prepolymers are used to produce high performance coatings and elastomers with optical clarity and hydrolysis resistance. Other aliphatic isocyanates include cyclohexane diisocyanate (CHDI), tetramethylxylene diisocyanate (TMXDI), and 1,3-bis(isocyanatomethyl)cyclohexane (H_6XDI).

Polyols

Polyols are higher molecular weight materials manufactured from an initiator and monomeric building blocks. They are most easily classified as polyether polyols, which are made by the reaction of epoxides (oxiranes) with an active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. They can be further classified according to their end use as flexible or rigid polyols, depending on the functionality of the initiator and their molecular weight. Taking into account functionality, flexible polyols have molecular weights from 2,000 to 10,000 (OH# from 18 to 56). Rigid polyols have molecular weights from 250 to 700 (OH# from 300 to 700). Polyols with molecular weights from 700 to 2,000 (OH# 60 to 280) are used to add stiffness or flexibility to base systems, as well as increase solubility of low molecular weight glycols in high molecular weight polyols.

Polyether polyols come in a wide variety of grades based on their end use, but are all constructed in a similar manner. Polyols for flexible applications use low functionality initiators such as dipropylene glycol (f=2), glycerine (f=3) or a sorbitol/water solution (f=2.75). Polyols for rigid applications use high functionality initiators such sucrose (f=8), sorbitol (f=6), toluenediamine (f=4), and Mannich bases (f=4). Propylene oxide is then added to the initiators until the desired molecular weight is achieved. Polyols extended with propylene oxide are terminated with secondary hydroxyl groups. In order to change the compatibility, rheological properties, and reactivity of a polyol, ethylene oxide is used as a co-reactant to create random or mixed block heteropolymers. Polyols capped with ethylene oxide contain a high percentage of primary hydroxyl groups, which are more reactive than secondary hydroxyl groups. Because of their high viscosity (470 OH# sucrose polyol, 33 Pa·s at 25 °C), carbohydrate initiated polyols often use glycerine or diethylene glycol as a co-initiate in order to lower the viscosity to ease handling and processing (490 OH# sucrose-glycerine polyol, 5.5 Pa·s at 25 °C). Graft polyols (also called filled polyols or polymer polyols) contain finely dispersed styrene-acrylonitrile, acrylonitrile, or polyurea (PHD) polymer solids chemically grafted to a high molecular weight polyether backbone. They are used to increase the load bearing properties of low-density high-resiliency (HR) foam, as well as add toughness to microcellular foams and cast elastomers. PHD polyols are also used to modify the combustion properties of HR flexible foam. Solids content ranges from 14% to 50%, with 22% and 43% being typical. Initiators such as ethylenediamine and triethanolamine are used to make low molecular weight rigid foam polyols that have built-in catalytic activity due to the presence of nitrogen atoms in the backbone. They are used to increase system reactivity and physical property build, and to reduce the friability of rigid foam molded parts. A special class of polyether polyols, poly(tetramethylene ether) glycols are made by polymerizing tetrahydrofuran. They are used in high performance coating and elastomer applications.

Polyester polyols fall into two distinct categories according to composition and application. Conventional polyester polyols are based on virgin raw materials and are manufactured by the direct polyesterification of high-purity diacids and glycols, such as adipic acid and 1,4-butanediol. They are distinguished by the choice of monomers, molecular weight, and degree of branching. While costly and difficult to handle because of their high viscosity, they offer physical properties not obtainable with polyether polyols, including superior solvent, abrasion, and cut resistance. Other polyester polyols are based on reclaimed raw materials. They are manufactured by transesterification (glycolysis) of recycled poly(ethyleneterephthalate) (PET) or dimethylterephthalate (DMT) distillation bottoms with glycols such as diethylene glycol. These low molecular weight, aromatic polyester polyols are used in the manufacture of rigid foam, and bring low cost and excellent flammability characteristics to polyisocyanurate (PIR) boardstock and polyurethane spray foam insulation.

Many polyols are polydispersive materials, being blends of two or more polyols each of specific molecular weights, to give intermediate molecular weight materials. It is not unusual to find blends of polyether and polyester polyols, to give specific compromises in properties.

Specialty polyols include polycarbonate polyols, polycaprolactone polyols, polybutadiene polyols, and polysulfide polyols. The materials are used in elastomer, sealant, and adhesive applications that require superior weatherability, and resistance to chemical and environmental attack. Natural oil polyols derived from castor oil and other vegetable oils are used to make elastomers, flexible bunstock, and flexible molded foam. Copolymerizing chlorotrifluoroethylene or tetrafluoroethylene with vinyl ethers containing hydroxyalkyl vinyl ether produces fluorinated (FEVE) polyols. Two component fluorinated polyurethane prepared by reacting FEVE fluorinated polyols with polyisocyanate have been applied for make ambient cure paint/coating. Since fluorinated polyurethanes contain high percentage of fluorine-carbon bond which is the strongest bond among all chemical bonds. Fluorinated polyurethanes have excellent resistance to UV, acids, alkali, salts, chemicals, solvents, weathering, corrosion, fugi and microbial attack. These have become the first choice for high performance coating/paints.

Chain extenders and cross linkers

Chain extenders (f=2) and cross linkers (f=3 or greater) are low molecular weight hydroxyl and amine terminated compounds that play an important role in the polymer morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains. This phase separation occurs because the mainly non-polar, low melting soft segments are incompatible with the polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values. The choice of chain extender also determines flexural, heat, and chemical resistance properties. The most important chain extenders are ethylene glycol, 1,4-butanediol (1,4-BDO or BDO), 1,6-hexanediol, cyclohexane dimethanol and hydroquinone bis(2-hydroxyethyl) ether (HQEE). All of these glycols form polyurethanes that phase separate well and form well defined hard segment domains, and are melt processable. They are all suitable for thermoplastic polyurethanes with the exception of ethylene glycol, since its derived bis-phenyl urethane undergoes unfavorable degradation at high hard segment levels. Diethanolamine and triethanolamine are used in flex molded foams to build firmness and add catalytic activity. Diethyltoluenediamine is used extensively in RIM, and in polyurethane and polyurea elastomer formulations.

table of chain extenders and cross linkers				
hydroxyl compounds – difunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
ethylene glycol	62.1	1.110	-13.4	197.4
diethylene glycol	106.1	1.111	-8.7	245.5
triethylene glycol	150.2	1.120	-7.2	287.8
tetraethylene glycol	194.2	1.123	-9.4	325.6
propylene glycol	76.1	1.032	supercools	187.4
dipropylene glycol	134.2	1.022	supercools	232.2
tripropylene glycol	192.3	1.110	supercools	265.1
1,3-propanediol	76.1	1.060	-28	210
1,3-butanediol	92.1	1.005	-	207.5
1,4-butanediol	92.1	1.017	20.1	235
neopentyl glycol	104.2	-	130	206
1,6-hexanediol	118.2	1.017	43	250
1,4-cyclohexanedimethanol	-	-	-	-
HQEE	-	-	-	-
ethanolamine	61.1	1.018	10.3	170
diethanolamine	105.1	1.097	28	271
methyldiethanolamine	119.1	1.043	-21	242
phenyldiethanolamine	181.2	-	58	228
hydroxyl compounds – trifunctional molecules				
	MW	**s.g.**	**f.p. °C**	**b.p. °C**

glycerol	92.1	1.261	18.0	290
trimethylolpropane	-	-	-	-
1,2,6-hexanetriol	-	-	-	-
triethanolamine	149.2	1.124	21	-
hydroxyl compounds – tetrafunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
pentaerythritol	136.2	-	260.5	-
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine	-	-	-	-
amine compounds – difunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
diethyltoluenediamine	178.3	1.022	-	308
dimethylthiotoluenediamine	214.0	1.208	-	-

Catalysts

Polyurethane catalysts can be classified into two broad categories, amine compounds and organometallic complexes. They can be further classified as to their specificity, balance, and relative power or efficiency. Traditional amine catalysts have been tertiary amines such as triethylenediamine (TEDA, also known as 1,4-diazabicyclo[2.2.2]octane or DABCO, an Air Products's trade mark), dimethylcyclohexylamine (DMCHA), and dimethylethanolamine (DMEA). Tertiary amine catalysts are selected based on whether they drive the urethane (polyol+isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction (e.g. using potassium acetate, to form isocyanurate ring structure). Since most tertiary amine catalysts will drive all three reactions to some extent, they are also selected based on how much they favor one reaction over another. For example, tetramethylbutanediamine (TMBDA) preferentially drives the gel reaction over the blow reaction. On the other hand, both pentamethyldipropylenetriamine and N-(3-dimethylaminopropyl)-N,N-diisopropanolamine balance the blow and gel reactions, although the former is more potent than the later on a weight basis. 1,3,5-(tris(3-dimethylamino)propyl)-hexahydro-s-triazine is a trimerization catalyst that also strongly drives the blow reaction. Molecular structure gives some clue to the strength and selectivity of the catalyst. Blow catalysts generally have an ether linkage two carbons away from a tertiary nitrogen. Examples include bis-(2-dimethylaminoethyl)ether (also known as A-99, formerly a Union Carbide product), and N-ethylmorpholine. Strong gel catalysts contain alkyl-substituted nitrogens, such as triethylamine (TEA), 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), and pentamethyldiethylenetriamine (PMDETA). Weaker gel catalysts contain ring-substituted nitrogens, such as benzyldimethylamine (BDMA). Trimerization catalysts contain the triazine structure, or are quaternary ammonium salts. Two trends have emerged since the late 1980s. The requirement to fill large, complex tooling with increasing production rates has led to the use of blocked catalysts to delay front end reactivity while maintaining back end cure. In the United States, acid- and quaternary ammonium salt-blocked TEDA and bis-(2-dimethylaminoethyl)ether are common blocked catalysts used in molded flexible foam and microcellular integral skin foam applications. Increasing aesthetic and environmental awareness has led to the use of non-fugitive catalysts for vehicle interior and furnishing applications in order to reduce odor, fogging, and the staining of vinyl coverings. Catalysts that contain a hydroxyl group or an active amino hydrogen, such as N,N,N'-trimethyl-N'-hydroxyethyl-bis(aminoethyl)ether and N'-(3-(dimethylamino)propyl)-N,N-dimethyl-1,3-propanediamine that react into the polymer matrix can replace traditional catalysts in these applications.

Organometallic compounds based on mercury, lead, tin (dibutyltin dilaurate), bismuth (bismuth octanoate), and zinc are used as polyurethane catalysts. Mercury carboxylates, such as phenylmercuric neodeconate, are particularly effective catalysts for polyurethane elastomer, coating and sealant applications, since they are very highly selective towards the polyol+isocyanate reaction. Mercury catalysts can be used at low levels to give systems a long pot life while still giving excellent back-end cure. Lead catalysts are used in highly reactive rigid spray foam insulation applications, since they maintain their potency in low temperature and high humidity conditions. Due to their toxicity and the necessity to dispose of mercury and lead catalysts and catalyzed material as hazardous waste in the United States, formulators have been searching for suitable replacements. Since the 1990s, bismuth and zinc carboxylates have been used as alternatives but have short comings of their own. In elastomer applications, long pot life systems do not build green strength as fast as mercury catalyzed systems. In spray foam applications, bismuth and zinc do not drive the front end fast enough in cold weather conditions and must be otherwise augmented to replace lead. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. For example, dibutyltin dilaurate is a standard catalyst for polyurethane adhesives and sealants, dioctyltin mercaptide is used in microcellular elastomer applications, and dibutyltin oxide is used in polyurethane paint and coating applications. Tin mercaptides are used in formulations that contain water, as tin carboxylates are susceptible to degradation from hydrolysis.

Surfactants

Surfactants are used to modify the characteristics of both foam and non-foam polyurethane polymers. They take the form of polydimethylsiloxane-polyoxyalkylene block copolymers, silicone oils, nonylphenol ethoxylates, and other organic compounds. In foams, they are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and sub-surface voids. In non-foam applications they are used as air release and anti-foaming agents, as wetting agents, and are used to eliminate surface defects such as pin holes, orange peel, and sink marks.

Production

The main polyurethane producing reaction is between a diisocyanate (aromatic and aliphatic types are available) and a polyol, typically a polypropylene glycol or polyester polyol, in the presence of catalysts and materials for controlling the cell structure, (surfactants) in the case of foams. Polyurethane can be made in a variety of densities and hardnesses by varying the type of monomer(s) used and adding other substances to modify their characteristics, notably density, or enhance their performance. Other additives can be used to improve the fire performance, stability in difficult chemical environments and other properties of the polyurethane products.

Health and safety

Fully reacted polyurethane polymer, CAS # 9009-54-5 (CAS registry number), is chemically inert. No exposure limits have been established by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity. Polyurethane polymer is a combustible solid and will ignite if exposed to an open flame. It begins to break down at about 240 °C (464 °F). Decomposition can produce isocyanates, carbon monoxide, nitrogen oxides, and hydrogen cyanide. Firefighters should wear self-contained breathing apparatus in enclosed areas. Polyurethane polymer dust can cause irritation to the eyes and lungs. Proper hygiene controls and personal protective equipment (PPE), such as gloves, dust masks, respirators, mechanical ventilation, and protective clothing and eye wear should be used.

Liquid resin blends and isocyanates may contain hazardous or regulated components. They should be handled in accordance with manufacturer recommendations found on product labels, and in MSDS (Material Safety Data Sheet) and product technical literature. Isocyanates are known skin and respiratory sensitizers, and proper engineering controls should be in place to prevent exposure to isocyanate liquid and vapor.

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. In Europe, health and safety information is available from ISOPA, the European Diisocyanate and Polyol Producers Association. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment).

Manufacturing

The methods of manufacturing polyurethane finished goods range from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Regardless of the end-product, the manufacturing principle is the same: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until a homogeneous blend is obtained, dispense the reacting liquid into a mold or on to a surface, wait until it cures, then demold the finished part.

Dispensing equipment

Although the capital outlay can be high, it is desirable to use a meter-mix or dispense unit for even low-volume production operations that require a steady output of finished parts. Dispense equipment consists of material holding (day) tanks, metering pumps, a mix head, and a control unit. Often, a conditioning or heater-chiller unit is added to control material temperature in order to improve mix efficiency, cure rate, and to reduce process variability. Choice of dispense equipment components depends on shot size, throughput, material characteristics such as viscosity and filler content, and process control. Material day tanks may be single to hundreds of gallons in size, and may be supplied directly from drums, IBCs (intermediate bulk containers, such as totes), or bulk storage tanks. They may incorporate level sensors, conditioning jackets, and mixers. Pumps can be sized to meter in single grams per second up to hundreds of pounds per minute. They can be rotary, gear, or piston pumps, or can be specially hardened lance pumps to meter liquids containing highly abrasive fillers such as wollastonite, chopped or hammer milled glass fibres.

A high pressure polyurethane dispense unit, showing control panel, high pressure pump, integral day tanks, and hydraulic drive unit.

A high pressure mix head, showing simple controls. Front view.

A high pressure mix head, showing material supply and hydraulic actuator lines. Rear view.

The pumps can drive low-pressure (10 to 30 bar, ~1 to 3 MPa) or high-pressure (125 to 250 bar, ~12.5 to 25.0 MPa) dispense systems. Mix heads can be simple static mix tubes, rotary element mixers, low-pressure dynamic mixers, or high-pressure hydraulically actuated direct impingement mixers. Control units may have basic on/off – dispense/stop switches, and analogue pressure and temperature gages, or may be computer controlled with flow meters to electronically calibrate mix ratio, digital temperature and level sensors, and a full suite of statistical process control software. Add-ons to dispense equipment include nucleation or gas injection units, and third or fourth stream capability for adding pigments or metering in supplemental additive packages.

A low pressure mix head with calibration chamber installed, showing material supply and air actuator lines

Low pressure mix head components, including mix chambers, conical mixers, and mounting plates

5-gallon (20-liter) material day tanks for supplying a low pressure dispense unit

Tooling

Distinct from pour-in-place, bun and boardstock, and coating applications, the production of piece parts requires some type of tooling to contain and form the reacting liquid. The choice of mold-making material is dependent on the expected number of uses to end-of-life (EOL), molding pressure, flexibility, and heat transfer characteristics. RTV silicone is used for tooling that has an EOL in the thousands of parts. It is typically used for molding rigid foam parts, where the ability to stretch and peel the mold around undercuts is needed. The heat transfer characteristic of RTV silicone tooling is poor. High-performance, flexible polyurethane elastomers are also used in this way.

Epoxy, metal-filled epoxy, and metal-coated epoxy is used for tooling that has an EOL in the tens-of-thousands of parts. It is typically used for molding flexible foam cushions and seating, integral skin and microcellular foam padding, and shallow-draft RIM bezels and fascia.

The heat transfer characteristic of epoxy tooling is fair; the heat transfer characteristic of metal-filled and metal-coated epoxy is good. Copper tubing can be incorporated into the body of the tool, allowing hot water to circulate and heat the mold surface. Aluminum is used for tooling that has an EOL in the hundreds-of-thousands of parts. It is typically used for molding microcellular foam gasketing and cast elastomer parts, and is milled or extruded into shape. Mirror-finish stainless steel is used for tooling that imparts a glossy appearance to the finished part. The heat transfer characteristic of metal tooling is excellent. Finally, molded or milled polypropylene is used to create low-volume tooling for molded gasket applications. Instead of many expensive metal molds, low-cost plastic tooling can be formed from a single metal master, which also allows greater design flexibility. The heat transfer characteristic of polypropylene tooling is poor, which must be taken into consideration during the formulation process.

Applications

In 2007, the global consumption of polyurethane raw materials was above 12 million metric tons, the average annual growth rate is about 5%.

Testing

Effects of visible light

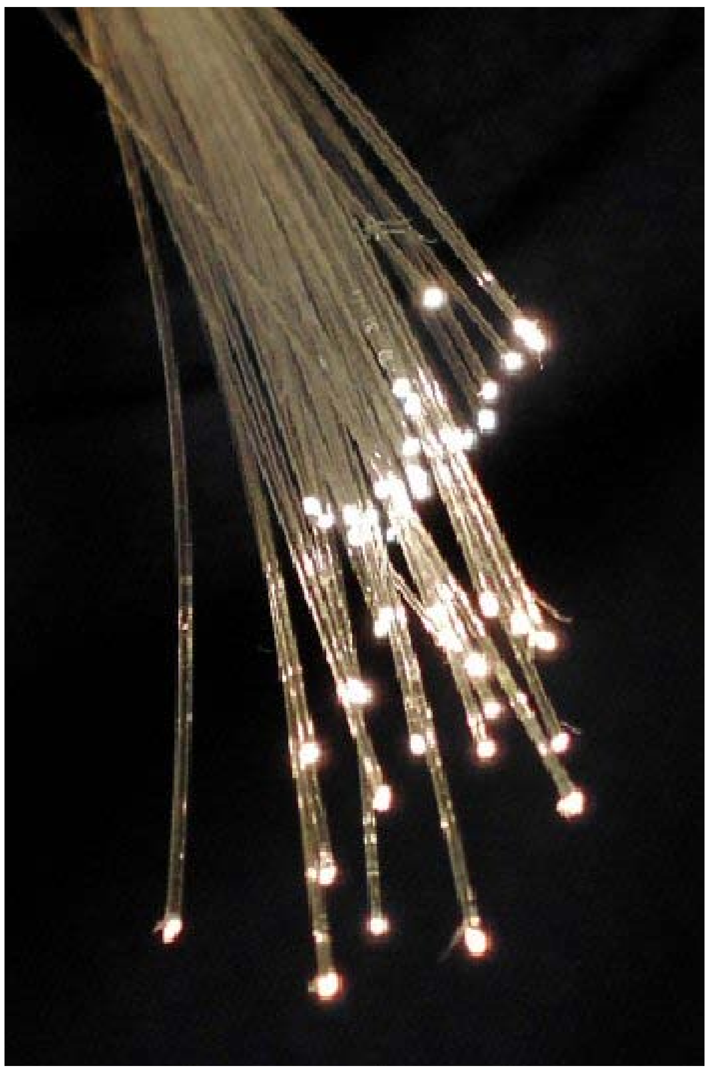
Polyurethanes, especially those made using aromatic isocyanates, contain chromophores which interact with light. This is of particular interest in the area of polyurethane coatings, where light stability is a critical factor and is the main reason that aliphatic isocyanates are used in making polyurethane coatings. When PU foam, which is made using aromatic isocyanates, is exposed to visible light it discolors, turning from off-white to yellow to reddish brown. It has been generally accepted that apart from yellowing, visible light has little effect on foam properties. This is especially the case if the yellowing happens on the outer portions of a large foam, as the deterioration of properties in the outer portion has little effect on the overall bulk properties of the foam itself.

It has been reported that exposure to visible light can affect the variability of some physical property test results. Increasing exposure time and/or light intensity during the storage of foam samples under ambient laboratory conditions increased the amount of permanent set induced in some compression set tests (the samples did not fully return to their original size and/or shape). Variability resulted from uncontrolled light exposure of cut samples prior to being compressed. Other foam properties were not substantively affected. It was recommended that specimen preparation and testing be done rapidly to minimize variation in results or if specimens are prepared but not tested for a week or more, that the samples should be protected from light exposure.

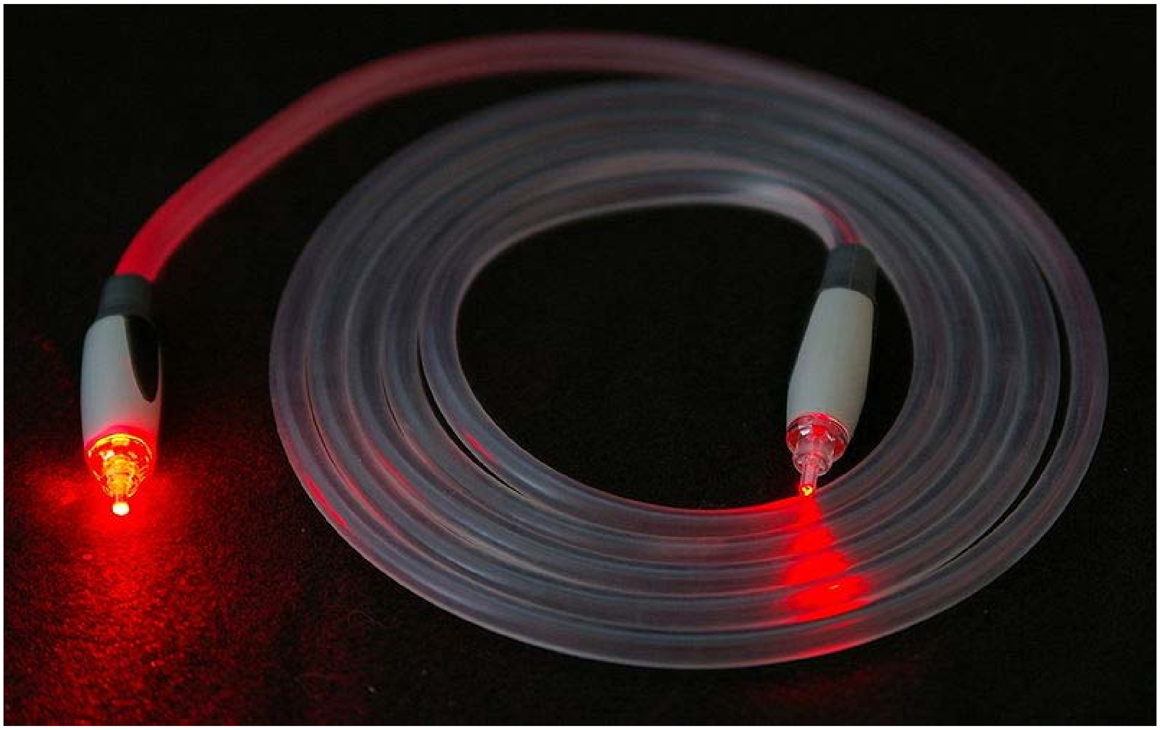
Higher-energy UV radiation promotes chemical reactions in foam, some of which are detrimental to the foam structure.

Chapter- 10

Optical Fiber



A bundle of optical fibers



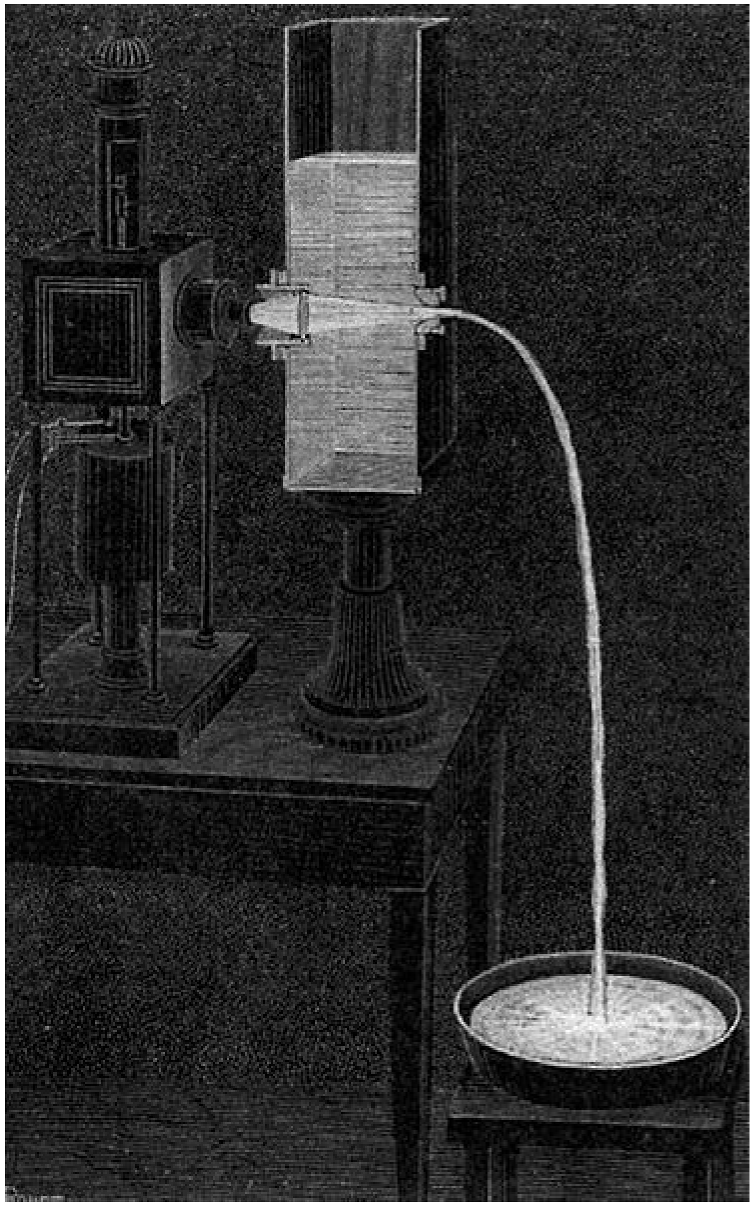
A TOSLINK fiber optic audio cable being illuminated at one end

An **optical fiber** or **optical fibre** is a thin, flexible, transparent fiber that acts as a waveguide, or "light pipe", to transmit light between the two ends of the fiber. The field of applied science and engineering concerned with the design and application of optical fibers is known as **fiber optics**. Optical fibers are widely used in fiber-optic communications, which permits transmission over longer distances and at higher bandwidths (data rates) than other forms of communication. Fibers are used instead of metal wires because signals travel along them with less loss and are also immune to electromagnetic interference. Fibers are also used for illumination, and are wrapped in bundles so they can be used to carry images, thus allowing viewing in tight spaces. Specially designed fibers are used for a variety of other applications, including sensors and fiber lasers.

Optical fiber typically consists of a transparent core surrounded by a transparent cladding material with a lower index of refraction. Light is kept in the core by total internal reflection. This causes the fiber to act as a waveguide. Fibers which support many propagation paths or transverse modes are called multi-mode fibers (MMF), while those which can only support a single mode are called single-mode fibers (SMF). Multi-mode fibers generally have a larger core diameter, and are used for short-distance communication links and for applications where high power must be transmitted. Single-mode fibers are used for most communication links longer than 1,050 meters (3,440 ft).

Joining lengths of optical fiber is more complex than joining electrical wire or cable. The ends of the fibers must be carefully cleaved, and then spliced together either mechanically or by fusing them together with heat. Special optical fiber connectors are used to make removable connections.

History



Daniel Colladon first described this "light fountain" or "light pipe" in an 1842 article titled *On the reflections of a ray of light inside a parabolic liquid stream*. This particular illustration comes from a later article by Colladon, in 1884.

Fiber optics, though used extensively in the modern world, is a fairly simple and old technology. Guiding of light by refraction, the principle that makes fiber optics possible, was first demonstrated by Daniel Colladon and Jacques Babinet in Paris in the early 1840s. John Tyndall included a demonstration of it in his public lectures in London a dozen years later. Tyndall also wrote about the property of total internal reflection in an introductory book about the nature of light in 1870: "When the light passes from air into water, the refracted ray is bent *towards* the perpendicular... When the ray passes from water to air it is bent *from* the perpendicular... If the angle which the ray in water encloses with the perpendicular to the surface be greater than 48 degrees, the ray will not quit the water at all: it will be *totally reflected* at the surface.... The angle which marks the limit where total reflection begins is called the limiting angle of the medium. For water this angle is 48°27', for flint glass it is 38°41', while for diamond it is 23°42'."

Practical applications, such as close internal illumination during dentistry, appeared early in the twentieth century. Image transmission through tubes was demonstrated independently by the radio experimenter Clarence Hansell and the television pioneer John Logie Baird in the 1920s. The principle was first used for internal medical examinations by Heinrich Lamm in the following decade. In 1952, physicist Narinder Singh Kapany conducted experiments that led to the invention of optical fiber. Modern optical fibers, where the glass fiber is coated with a transparent cladding to offer a more suitable refractive index, appeared later in the decade. Development then focused on fiber bundles for image transmission. The first fiber optic semi-flexible gastroscope was patented by Basil Hirschowitz, C. Wilbur Peters, and Lawrence E. Curtiss, researchers at the University of Michigan, in 1956. In the process of developing the gastroscope, Curtiss produced the first glass-clad fibers; previous optical fibers had relied on air or impractical oils and waxes as the low-index cladding material. A variety of other image transmission applications soon followed.

In the late 19th and early 20th centuries, light was guided through bent glass rods to illuminate body cavities. Alexander Graham Bell invented a 'Photophone' to transmit voice signals over an optical beam.

Jun-ichi Nishizawa, a Japanese scientist at Tohoku University, also proposed the use of optical fibers for communications in 1963, as stated in his book published in 2004 in India. Nishizawa invented other technologies which contributed to the development of optical fiber communications, such as the graded-index optical fiber as a channel for transmitting light from semiconductor lasers. Charles K. Kao and George A. Hockham of the British company Standard Telephones and Cables (STC) were the first to promote the idea that the attenuation in optical fibers could be reduced below 20 decibels per kilometer (dB/km), allowing fibers to be a practical medium for communication. They proposed that the attenuation in fibers available at the time was caused by impurities, which could be removed, rather than fundamental physical effects such as scattering. They correctly and systematically theorized the light-loss properties for optical fiber, and pointed out the right material to manufacture such fibers — silica glass with high purity. This discovery led to Kao being awarded the Nobel Prize in Physics in 2009.

NASA used fiber optics in the television cameras sent to the moon. At the time such use in the cameras was 'classified confidential' and only those with the right security clearance or those accompanied by someone with the right security clearance were permitted to handle the cameras.

The crucial attenuation limit of 20 dB/km was first achieved in 1970, by researchers Robert D. Maurer, Donald Keck, Peter C. Schultz, and Frank Zimar working for American glass maker Corning Glass Works, now Corning Incorporated. They demonstrated a fiber with 17 dB/km attenuation by doping silica glass with titanium. A few years later they produced a fiber with only 4 dB/km attenuation using germanium dioxide as the core dopant. Such low attenuation ushered in optical fiber telecommunication. In 1981, General Electric produced fused quartz ingots that could be drawn into fiber optic strands 25 miles (40 km) long.

Attenuation in modern optical cables is far less than in electrical copper cables, leading to long-haul fiber connections with repeater distances of 70–150 kilometers (43–93 mi). The erbium-doped fiber amplifier, which reduced the cost of long-distance fiber systems by reducing or eliminating optical-electrical-optical repeaters, was co-developed by teams led by David N. Payne of the University of Southampton and Emmanuel Desurvire at Bell Labs in 1986. Robust modern optical fiber uses glass for both core and sheath and is therefore less prone to aging processes. It was invented by Gerhard Bernsee of Schott Glass in Germany in 1973.

The emerging field of photonic crystals led to the development in 1991 of photonic-crystal fiber which guides light by diffraction from a periodic structure, rather than by total internal reflection. The first photonic crystal fibers became commercially available in 2000. Photonic crystal fibers can carry higher power than conventional fibers and their wavelength-dependent properties can be manipulated to improve performance.

Applications

Optical fiber communication

Optical fiber can be used as a medium for telecommunication and networking because it is flexible and can be bundled as cables. It is especially advantageous for long-distance communications, because light propagates through the fiber with little attenuation compared to electrical cables. This allows long distances to be spanned with few repeaters. Additionally, the per-channel light signals propagating in the fiber have been modulated at rates as high as 111 gigabits per second by NTT, although 10 or 40 Gbit/s is typical in deployed systems. Each fiber can carry many independent channels, each using a different wavelength of light (wavelength-division multiplexing (WDM)). The net data rate (data rate without overhead bytes) per fiber is the per-channel data rate reduced by the FEC overhead, multiplied by the number of channels (usually up to eighty in commercial dense WDM systems as of 2008). The current laboratory fiber optic data rate record, held by Bell Labs in Villarceaux, France, is multiplexing 155 channels, each carrying 100 Gbit/s over a 7000 km fiber. Nippon Telegraph and Telephone Corporation have also managed 69.1 Tbit/s over a single 240 km fiber (multiplexing 432 channels, equating to 171 Gbit/s per channel). Bell Labs also broke a 100 Petabit per second *kilometer* barrier (15.5 Tbit/s over a single 7000 km fiber).

For short distance applications, such as creating a network within an office building, fiber-optic cabling can be used to save space in cable ducts. This is because a single fiber can often carry much more data than many electrical cables, such as 4 pair Cat-5 Ethernet cabling. Fiber is also immune to electrical interference; there is no cross-talk between signals in different cables and no pickup of environmental noise. Non-armored fiber cables do not conduct electricity, which makes fiber a good solution for protecting communications equipment located in high voltage environments such as power generation facilities, or metal communication structures prone to lightning strikes. They can also be used in environments where explosive fumes are present, without danger of ignition. Wiretapping is more difficult compared to electrical connections, and there are concentric dual core fibers that are said to be tap-proof.

Fiber optic sensors

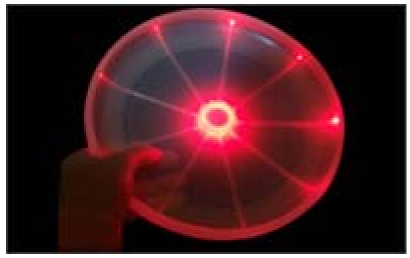
Fibers have many uses in remote sensing. In some applications, the sensor is itself an optical fiber. In other cases, fiber is used to connect a non-fiberoptic sensor to a measurement system. Depending on the application, fiber may be used because of its small size, or the fact that no electrical power is needed at the remote location, or because many sensors can be multiplexed along the length of a fiber by using different wavelengths of light for each sensor, or by sensing the time delay as light passes along the fiber through each sensor. Time delay can be determined using a device such as an optical time-domain reflectometer.

Optical fibers can be used as sensors to measure strain, temperature, pressure and other quantities by modifying a fiber so that the quantity to be measured modulates the intensity, phase, polarization, wavelength or transit time of light in the fiber. Sensors that vary the intensity of light are the simplest, since only a simple source and detector are required. A particularly useful feature of such fiber optic sensors is that they can, if required, provide distributed sensing over distances of up to one meter.

Extrinsic fiber optic sensors use an optical fiber cable, normally a multi-mode one, to transmit modulated light from either a non-fiber optical sensor, or an electronic sensor connected to an optical transmitter. A major benefit of extrinsic sensors is their ability to reach places which are otherwise inaccessible. An example is the measurement of temperature inside aircraft jet engines by using a fiber to transmit radiation into a radiation pyrometer located outside the engine. Extrinsic sensors can also be used in the same way to measure the internal temperature of electrical transformers, where the extreme electromagnetic fields present make other measurement techniques impossible. Extrinsic sensors are used to measure vibration, rotation, displacement, velocity, acceleration, torque, and twisting. A solid state version of the gyroscope using the interference of light has been developed. The fiber optic gyroscope (FOG) has no moving parts and exploits the Sagnac effect to detect mechanical rotation.

A common use for fiber optic sensors are in advanced intrusion detection security systems, where the light is transmitted along the fiber optic sensor cable, which is placed on a fence, pipeline or communication cabling, and the returned signal is monitored and analysed for disturbances. This return signal is digitally processed to identify if there is a disturbance, and if an intrusion has occurred an alarm is triggered by the fiber optic security system.

Other uses of optical fibers



A frisbee illuminated by fiber optics

Light reflected from optical fiber illuminates exhibited model

Fiber optic front sight on a hand gun

Fibers are widely used in illumination applications. They are used as light guides in medical and other applications where bright light needs to be shone on a target without a clear line-of-sight path. In some buildings, optical fibers are used to route sunlight from the roof to other parts of the building. Optical fiber illumination is also used for decorative applications, including signs, art, and artificial Christmas trees. Swarovski boutiques use optical fibers to illuminate their crystal showcases from many different angles while only employing one light source. Optical fiber is an intrinsic part of the light-transmitting concrete building product, LiTraCon.

Optical fiber is also used in imaging optics. A coherent bundle of fibers is used, sometimes along with lenses, for a long, thin imaging device called an endoscope, which is used to view objects through a small hole. Medical endoscopes are used for minimally invasive exploratory or surgical procedures (endoscopy). Industrial endoscopes are used for inspecting anything hard to reach, such as jet engine interiors.

In spectroscopy, optical fiber bundles are used to transmit light from a spectrometer to a substance which cannot be placed inside the spectrometer itself, in order to analyze its composition. A spectrometer analyzes substances by bouncing light off of and through them. By using fibers, a spectrometer can be used to study objects that are too large to fit inside, or gasses, or reactions which occur in pressure vessels.

An optical fiber doped with certain rare earth elements such as erbium can be used as the gain medium of a laser or optical amplifier. Rare-earth doped optical fibers can be used to provide signal amplification by splicing a short section of doped fiber into a regular (undoped) optical fiber line. The doped fiber is optically pumped with a second laser wavelength that is coupled into the line in addition to the signal wave. Both wavelengths of light are transmitted through the doped fiber, which transfers energy from the second pump wavelength to the signal wave. The process that causes the amplification is stimulated emission.

Optical fibers doped with a wavelength shifter are used to collect scintillation light in physics experiments.

Optical fiber can be used to supply a low level of power (around one watt) to electronics situated in a difficult electrical environment. Examples of this are electronics in high-powered antenna elements and measurement devices used in high voltage transmission equipment.

A growing trend in iron sights for arms, is the use of short pieces of optical fiber for contrast enhancement dots, made in such a way that ambient light falling on the length of the fiber is concentrated at the tip, making the dots slightly brighter than the surroundings. This method is most commonly used in front sights, but many makers offer sights that use fiber optics on front and rear sights. Fiber optic sights can now be found on handguns, rifles, and shotguns, both as aftermarket accessories and a growing number of factory guns.

Principle of operation

An optical fiber is a cylindrical dielectric waveguide (nonconducting waveguide) that transmits light along its axis, by the process of total internal reflection. The fiber consists of a *core* surrounded by a cladding layer, both of which are made of dielectric materials. To confine the optical signal in the core, the refractive index of the core must be greater than that of the cladding. The boundary between the core and cladding may either be abrupt, in *step-index fiber*, or gradual, in *graded-index fiber*.

Index of refraction

The index of refraction is a way of measuring the speed of light in a material. Light travels fastest in a vacuum, such as outer space. The speed of light in a vacuum is about 300,000 kilometres (186 thousand miles) per second. Index of refraction is calculated by dividing the speed of light in a vacuum by the speed of light in some other medium. The index of refraction of a vacuum is therefore 1, by definition. The typical value for the cladding of an optical fiber is 1.46. The core value is typically 1.48. The larger the index of refraction, the slower light travels in that medium. From this information, a good rule of thumb is that signal using optical fiber for communication will travel at around 200 million meters per second. Or to put it another way, to travel 1000 kilometers in fiber, the signal will take 5 milliseconds to propagate. Thus a phone call carried by fiber between

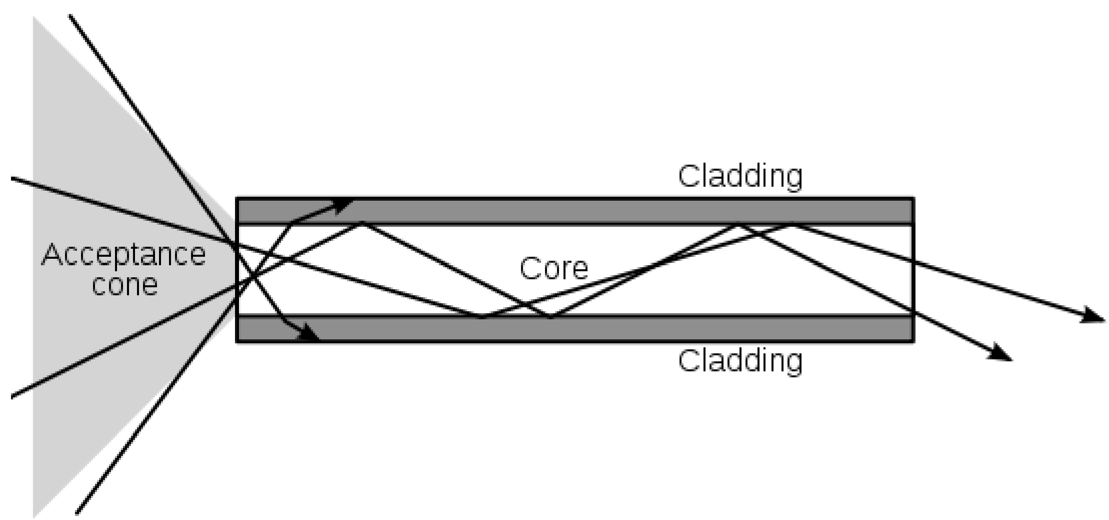
Sydney and New York, a 12000 kilometer distance, means that there is an absolute minimum delay of 60 milliseconds (or around 1/16th of a second) between when one caller speaks to when the other hears. (Of course the fiber in this case will probably travel a longer route, and there will be additional delays due to communication equipment switching and the process of encoding and decoding the voice onto the fiber).

Total internal reflection

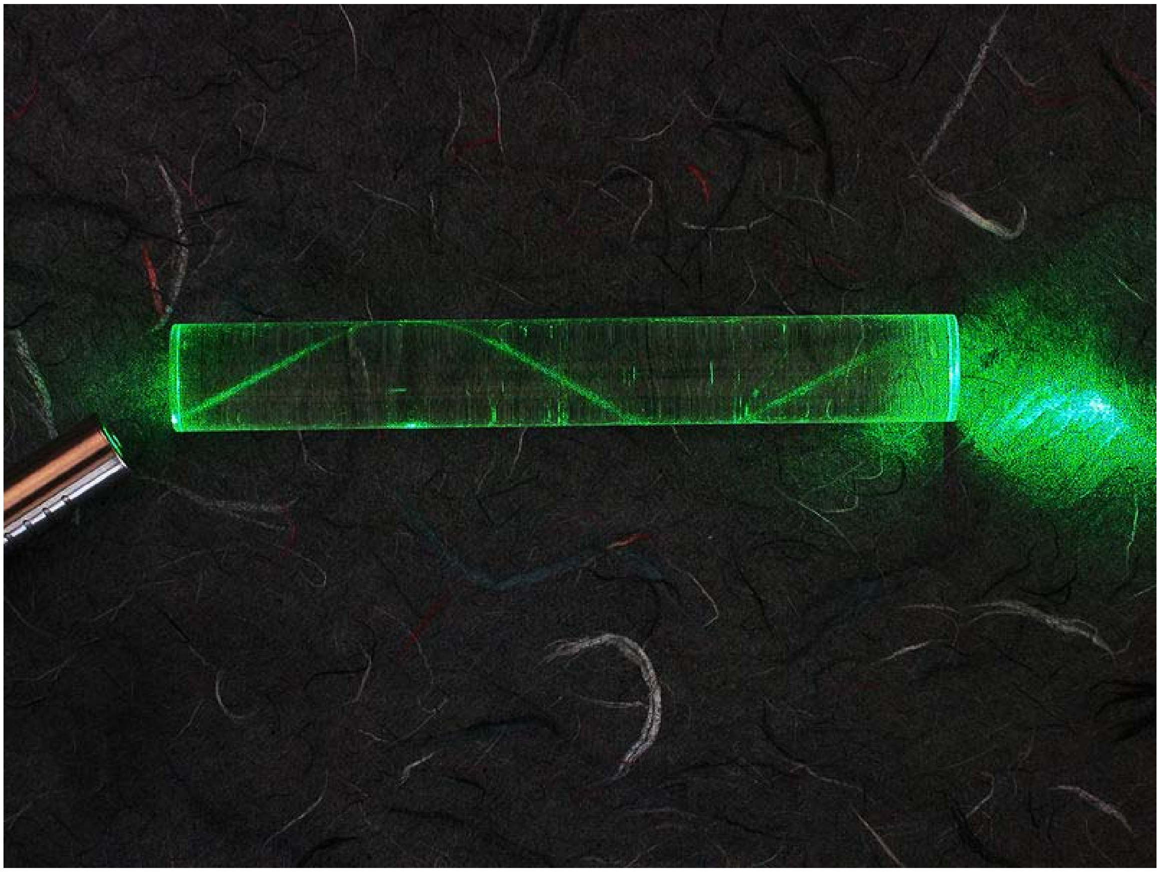
When light traveling in a dense medium hits a boundary at a steep angle (larger than the "critical angle" for the boundary), the light will be completely reflected. This effect is used in optical fibers to confine light in the core. Light travels along the fiber bouncing back and forth off of the boundary. Because the light must strike the boundary with an angle greater than the critical angle, only light that enters the fiber within a certain range of angles can travel down the fiber without leaking out. This range of angles is called the acceptance cone of the fiber. The size of this acceptance cone is a function of the refractive index difference between the fiber's core and cladding.

In simpler terms, there is a maximum angle from the fiber axis at which light may enter the fiber so that it will propagate, or travel, in the core of the fiber. The sine of this maximum angle is the numerical aperture (NA) of the fiber. Fiber with a larger NA requires less precision to splice and work with than fiber with a smaller NA. Single-mode fiber has a small NA.

Multi-mode fiber

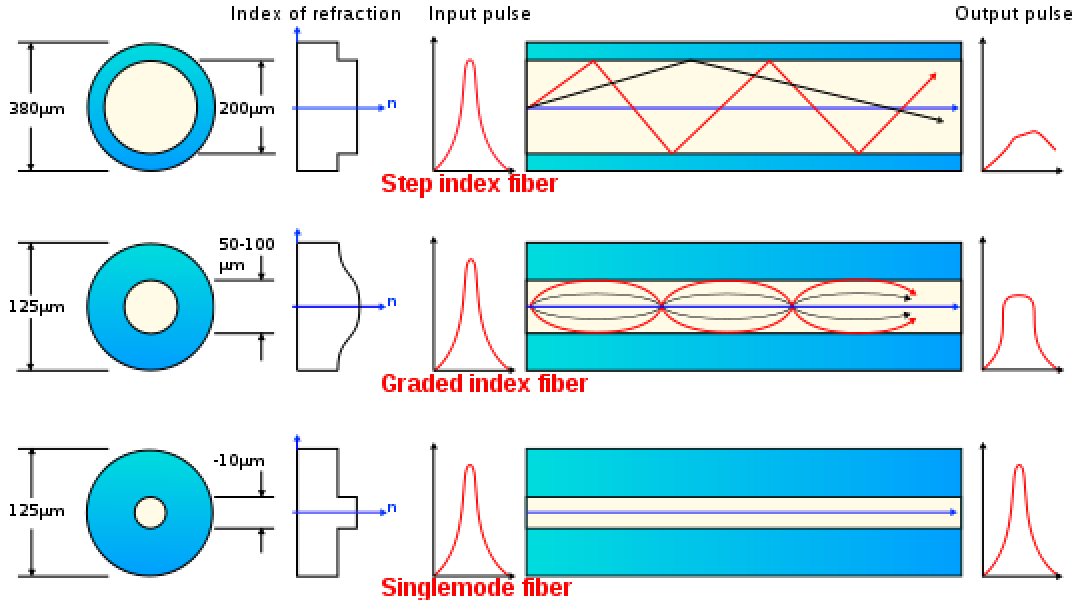


The propagation of light through a multi-mode optical fiber



A laser bouncing down an acrylic rod, illustrating the total internal reflection of light in a multi-mode optical fiber.

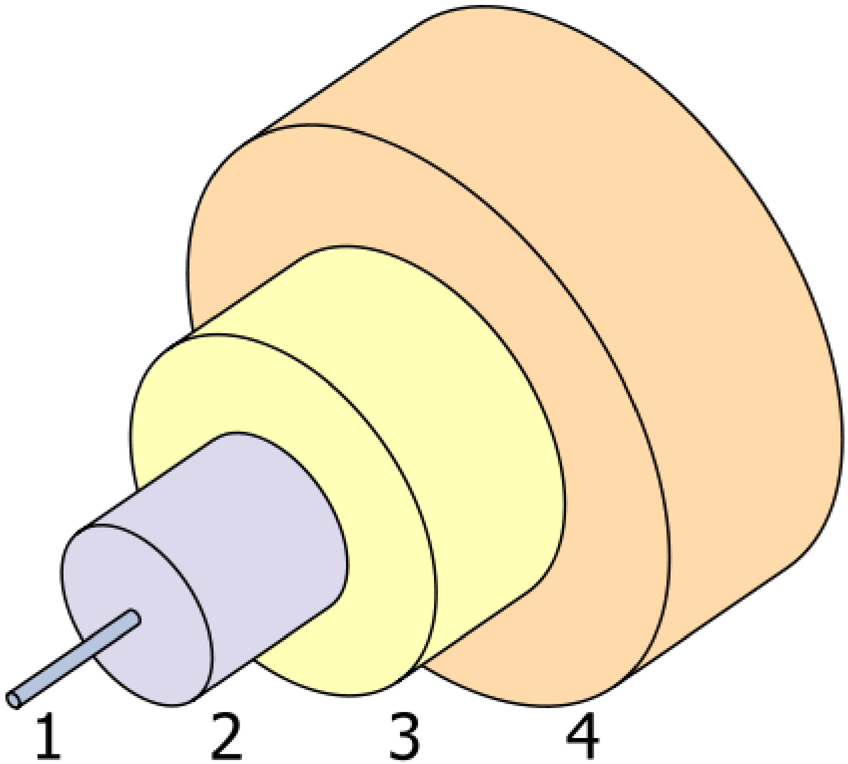
Fiber with large core diameter (greater than 10 micrometers) may be analyzed by geometrical optics. Such fiber is called *multi-mode fiber*, from the electromagnetic analysis (see below). In a step-index multi-mode fiber, rays of light are guided along the fiber core by total internal reflection. Rays that meet the core-cladding boundary at a high angle (measured relative to a line normal to the boundary), greater than the critical angle for this boundary, are completely reflected. The critical angle (minimum angle for total internal reflection) is determined by the difference in index of refraction between the core and cladding materials. Rays that meet the boundary at a low angle are refracted from the core into the cladding, and do not convey light and hence information along the fiber. The critical angle determines the acceptance angle of the fiber, often reported as a numerical aperture. A high numerical aperture allows light to propagate down the fiber in rays both close to the axis and at various angles, allowing efficient coupling of light into the fiber. However, this high numerical aperture increases the amount of dispersion as rays at different angles have different path lengths and therefore take different times to traverse the fiber.



Optical fiber types

In graded-index fiber, the index of refraction in the core decreases continuously between the axis and the cladding. This causes light rays to bend smoothly as they approach the cladding, rather than reflecting abruptly from the core-cladding boundary. The resulting curved paths reduce multi-path dispersion because high angle rays pass more through the lower-index periphery of the core, rather than the high-index center. The index profile is chosen to minimize the difference in axial propagation speeds of the various rays in the fiber. This ideal index profile is very close to a parabolic relationship between the index and the distance from the axis.

Single-mode fiber



The structure of a typical single-mode fiber.
1. Core: 8 µm diameter
2. Cladding: 125 µm dia.
3. Buffer: 250 µm dia.
4. Jacket: 400 µm dia.

Fiber with a core diameter less than about ten times the wavelength of the propagating light cannot be modeled using geometric optics. Instead, it must be analyzed as an electromagnetic structure, by solution of Maxwell's equations as reduced to the electromagnetic wave equation. The electromagnetic analysis may also be required to understand behaviors such as speckle that occur when coherent light propagates in multi-mode fiber. As an optical waveguide, the fiber supports one or more confined transverse modes by which light can propagate along the fiber. Fiber supporting only one mode is called *single-mode* or *mono-mode fiber*. The behavior of larger-core multi-mode fiber can also be modeled using the wave equation, which shows that such fiber supports more than one mode of propagation (hence the name). The results of such modeling of multi-mode fiber approximately agree with the predictions of geometric optics, if the fiber core is large enough to support more than a few modes.

The waveguide analysis shows that the light energy in the fiber is not completely confined in the core. Instead, especially in single-mode fibers, a significant fraction of the energy in the bound mode travels in the cladding as an evanescent wave.

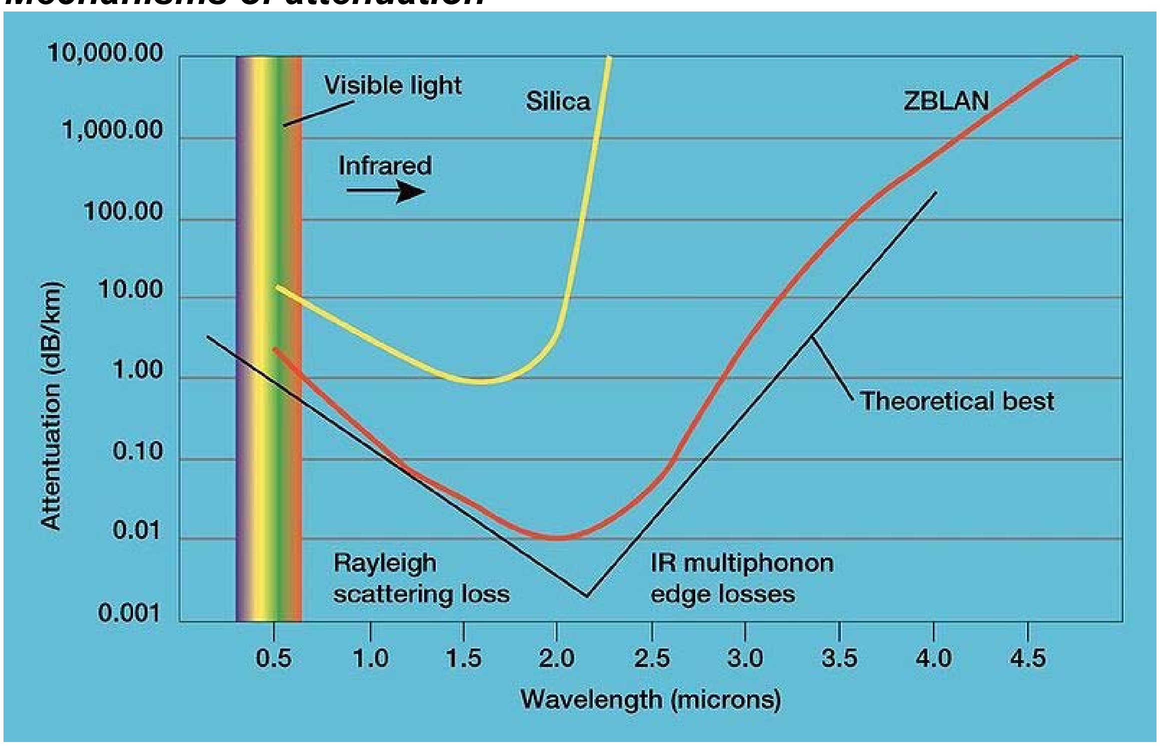
The most common type of single-mode fiber has a core diameter of 8–10 micrometers and is designed for use in the near infrared. The mode structure depends on the wavelength of the light used, so that this fiber actually supports a small number of additional modes at visible wavelengths. Multi-mode fiber, by comparison, is manufactured with core diameters as small as 50 micrometers and as large as hundreds of micrometers. The normalized frequency V for this fiber should be less than the first zero of the Bessel function J_0 (approximately 2.405).

Special-purpose fiber

Some special-purpose optical fiber is constructed with a non-cylindrical core and/or cladding layer, usually with an elliptical or rectangular cross-section. These include polarization-maintaining fiber and fiber designed to suppress whispering gallery mode propagation.

Photonic-crystal fiber is made with a regular pattern of index variation (often in the form of cylindrical holes that run along the length of the fiber). Such fiber uses diffraction effects instead of or in addition to total internal reflection, to confine light to the fiber's core. The properties of the fiber can be tailored to a wide variety of applications.

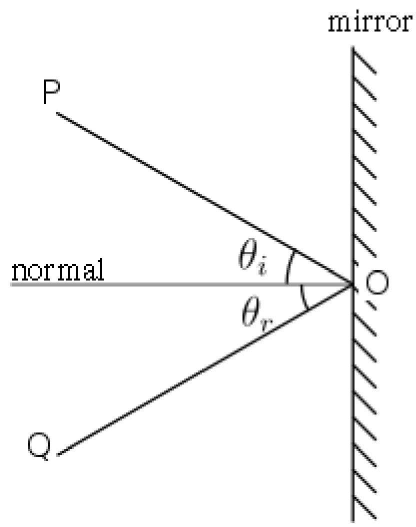
Mechanisms of attenuation



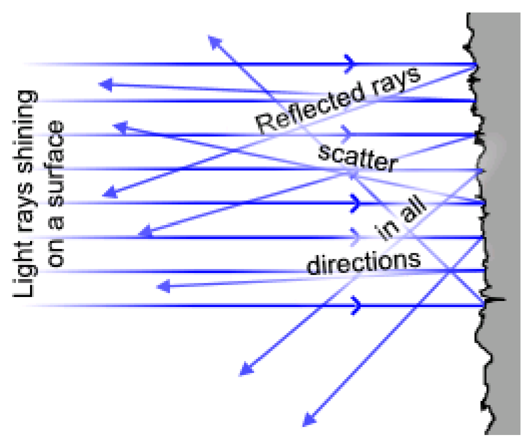
Light attenuation by ZBLAN and silica fibers

Attenuation in fiber optics, also known as transmission loss, is the reduction in intensity of the light beam (or signal) with respect to distance traveled through a transmission medium. Attenuation coefficients in fiber optics usually use units of dB/km through the medium due to the relatively high quality of transparency of modern optical transmission media. The medium is usually a fiber of silica glass that confines the incident light beam to the inside. Attenuation is an important factor limiting the transmission of a digital signal across large distances. Thus, much research has gone into both limiting the attenuation and maximizing the amplification of the optical signal. Empirical research has shown that attenuation in optical fiber is caused primarily by both scattering and absorption.

Light scattering



Specular reflection



Diffuse reflection

The propagation of light through the core of an optical fiber is based on total internal reflection of the lightwave. Rough and irregular surfaces, even at the molecular level, can cause light rays to be reflected in random directions. This is called diffuse reflection or scattering, and it is typically characterized by wide variety of reflection angles.

Light scattering depends on the wavelength of the light being scattered. Thus, limits to spatial scales of visibility arise, depending on the frequency of the incident light-wave and the physical dimension (or spatial scale) of the scattering center, which is typically in the form of some specific micro-structural feature. Since visible light has a wavelength of the order of one micrometre (one millionth of a meter) scattering centers will have dimensions on a similar spatial scale.

Thus, attenuation results from the incoherent scattering of light at internal surfaces and interfaces. In (poly)crystalline materials such as metals and ceramics, in addition to pores, most of the internal surfaces or interfaces are in the form of grain boundaries that separate tiny regions of crystalline order. It has recently been shown that when the size of the scattering center (or grain boundary) is reduced below the size of the wavelength of the light being scattered, the scattering no longer occurs to any significant extent. This phenomenon has given rise to the production of transparent ceramic materials.

Similarly, the scattering of light in optical quality glass fiber is caused by molecular level irregularities (compositional fluctuations) in the glass structure. Indeed, one emerging school of thought is that a glass is simply the limiting case of a polycrystalline solid. Within this framework, "domains" exhibiting various degrees of short-range order become the building blocks of both metals and alloys, as well as glasses and ceramics. Distributed both between and within these domains are micro-structural defects which will provide the most ideal locations for the occurrence of light scattering. This same phenomenon is seen as one of the limiting factors in the transparency of IR missile domes.

At high optical powers, scattering can also be caused by nonlinear optical processes in the fiber.

UV-Vis-IR absorption

In addition to light scattering, attenuation or signal loss can also occur due to selective absorption of specific wavelengths, in a manner similar to that responsible for the appearance of color. Primary material considerations include both electrons and molecules as follows:

1) At the electronic level, it depends on whether the electron orbitals are spaced (or "quantized") such that they can absorb a quantum of light (or photon) of a specific wavelength or frequency in the ultraviolet (UV) or visible ranges. This is what gives rise to color.

2) At the atomic or molecular level, it depends on the frequencies of atomic or molecular vibrations or chemical bonds, how close-packed its atoms or molecules are, and whether or not the atoms or molecules exhibit long-range order. These factors will determine the capacity of the material transmitting longer wavelengths in the infrared (IR), far IR, radio and microwave ranges.

The design of any optically transparent device requires the selection of materials based upon knowledge of its properties and limitations. The lattice absorption characteristics observed at the lower frequency regions (mid IR to far-infrared wavelength range) define the long-wavelength transparency limit of the material. They are the result of the interactive coupling between the motions of thermally induced vibrations of the constituent atoms and molecules of the solid lattice and the incident light wave radiation. Hence, all materials are bounded by limiting regions of absorption caused by atomic and molecular vibrations (bond-stretching)in the far-infrared (>10 µm).

Thus, multi-phonon absorption occurs when two or more phonons simultaneously interact to produce electric dipole moments with which the incident radiation may couple. These dipoles can absorb energy from the incident radiation, reaching a maximum coupling with the radiation when the frequency is equal to the fundamental vibrational mode of the molecular dipole (e.g. Si-O bond) in the far-infrared, or one of its harmonics.

The selective absorption of infrared (IR) light by a particular material occurs because the selected frequency of the light wave matches the frequency (or an integer multiple of the frequency) at which the particles of that material vibrate. Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared (IR) light.

Reflection and transmission of light waves occur because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. When IR light of these frequencies strikes an object, the energy is either reflected or transmitted.

Manufacturing

Materials

Glass optical fibers are almost always made from silica, but some other materials, such as fluorozirconate, fluoroaluminate, and chalcogenide glasses as well as crystalline materials like sapphire, are used for longer-wavelength infrared or other specialized applications. Silica and fluoride glasses usually have refractive indices of about 1.5, but some materials such as the chalcogenides can have indices as high as 3. Typically the index difference between core and cladding is less than one percent.

Plastic optical fibers (POF) are commonly step-index multi-mode fibers with a core diameter of 0.5 millimeters or larger. POF typically have higher attenuation coefficients than glass fibers, 1 dB/m or higher, and this high attenuation limits the range of POF-based systems.

Silica

Silica exhibits fairly good optical transmission over a wide range of wavelengths. In the near-infrared (near IR) portion of the spectrum, particularly around 1.5 µm, silica can have extremely low absorption and scattering losses of the order of 0.2 dB/km. A high transparency in the 1.4-μm region is achieved by maintaining a low concentration of hydroxyl groups (OH). Alternatively, a high OH concentration is better for transmission in the ultraviolet (UV) region.

Silica can be drawn into fibers at reasonably high temperatures, and has a fairly broad glass transformation range. One other advantage is that fusion splicing and cleaving of silica fibers is relatively effective. Silica fiber also has high mechanical strength against both pulling and even bending, provided that the fiber is not too thick and that the surfaces have been well prepared during processing. Even simple cleaving (breaking) of the ends of the fiber can provide nicely flat surfaces with acceptable optical quality. Silica is also relatively chemically inert. In particular, it is not hygroscopic (does not absorb water).

Silica glass can be doped with various materials. One purpose of doping is to raise the refractive index (e.g. with Germanium dioxide (GeO_2) or Aluminium oxide (Al_2O_3)) or to lower it (e.g. with fluorine or Boron trioxide (B_2O_3)). Doping is also possible with laser-active ions (for example, rare earth-doped fibers) in order to obtain active fibers to be used, for example, in fiber amplifiers or laser applications. Both the fiber core and cladding are typically doped, so that the entire assembly (core and cladding) is effectively the same compound (e.g. an aluminosilicate, germanosilicate, phosphosilicate or borosilicate glass).

Particularly for active fibers, pure silica is usually not a very suitable host glass, because it exhibits a low solubility for rare earth ions. This can lead to quenching effects due to clustering of dopant ions. Aluminosilicates are much more effective in this respect.

Silica fiber also exhibits a high threshold for optical damage. This property ensures a low tendency for laser-induced breakdown. This is important for fiber amplifiers when utilized for the amplification of short pulses.

Because of these properties silica fibers are the material of choice in many optical applications, such as communications (except for very short distances with plastic optical fiber), fiber lasers, fiber amplifiers, and fiber-optic sensors. The large efforts which have been put forth in the development of various types of silica fibers have further increased the performance of such fibers over other materials.

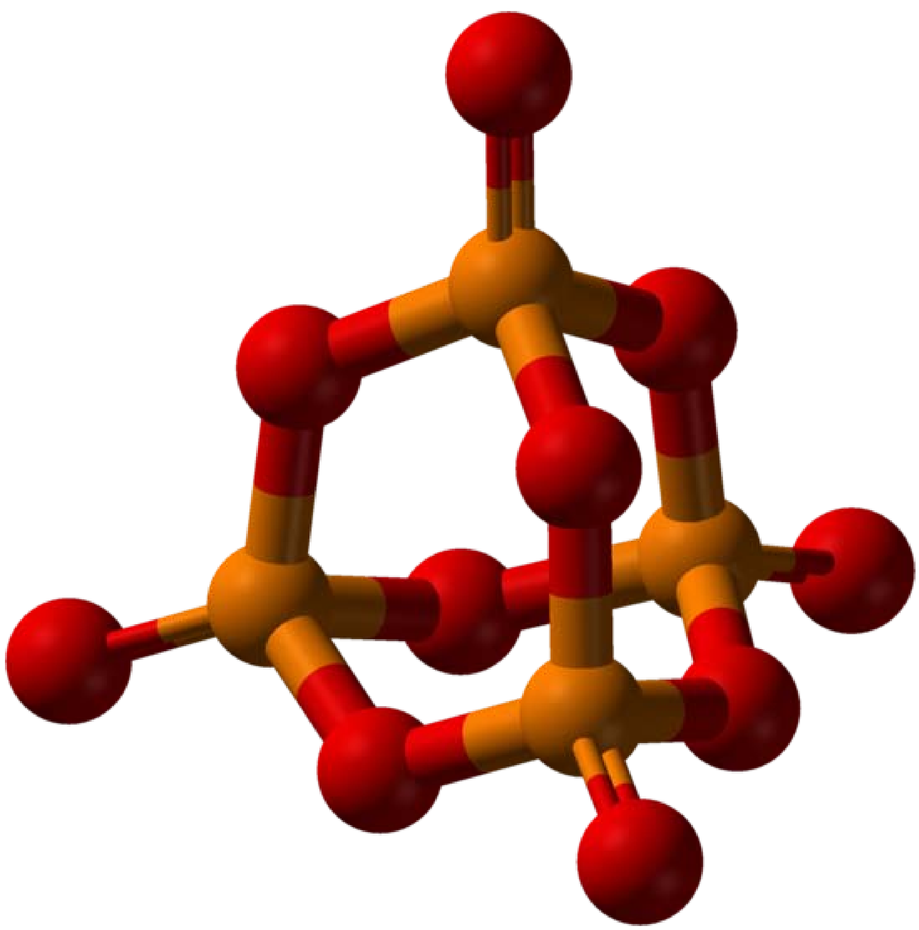
Fluorides

Fluoride glass is a class of non-oxide optical quality glasses composed of fluorides of various metals. Because of their low viscosity, it is very difficult to completely avoid crystallization while processing it through the glass transition (or drawing the fiber from the melt). Thus, although heavy metal fluoride glasses (HMFG) exhibit very low optical attenuation, they are not only difficult to manufacture, but are quite fragile, and have poor resistance to moisture and other environmental attacks. Their best attribute is that they lack the absorption band associated with the hydroxyl (OH) group (3200–3600 cm^{-1}), which is present in nearly all oxide-based glasses.

An example of a heavy metal fluoride glass is the ZBLAN glass group, composed of zirconium, barium, lanthanum, aluminium, and sodium fluorides. Their main technological application is as optical waveguides in both planar and fiber form. They are advantageous especially in the mid-infrared (2000–5000 nm) range.

HMFGs were initially slated for optical fiber applications, because the intrinsic losses of a mid-IR fiber could in principle be lower than those of silica fibers, which are transparent only up to about 2 µm. However, such low losses were never realized in practice, and the fragility and high cost of fluoride fibers made them less than ideal as primary candidates. Later, the utility of fluoride fibers for various other applications was discovered. These include mid-IR spectroscopy, fiber optic sensors, thermometry, and imaging. Also, fluoride fibers can be used for guided lightwave transmission in media such as YAG (yttria-alumina garnet) lasers at 2.9 µm, as required for medical applications (e.g. ophthalmology and dentistry).

Phosphates



The P_4O_{10} cagelike structure—the basic building block for phosphate glass

Phosphate glass constitutes a class of optical glasses composed of metaphosphates of various metals. Instead of the SiO_4 tetrahedra observed in silicate glasses, the building block for this glass former is Phosphorus pentoxide (P_2O_5), which crystallizes in at least four different forms. The most familiar polymorph (see figure) comprises molecules of P_4O_{10}.

Phosphate glasses can be advantageous over silica glasses for optical fibers with a high concentration of doping rare earth ions. A mix of fluoride glass and phosphate glass is fluorophosphate glass.

Chalcogenides

The chalcogens—the elements in group 16 of the periodic table—particularly sulfur (S), selenium (Se) and tellurium (Te)—react with more electropositive elements, such as silver, to form chalcogenides. These are extremely versatile compounds, in that they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons.

Process

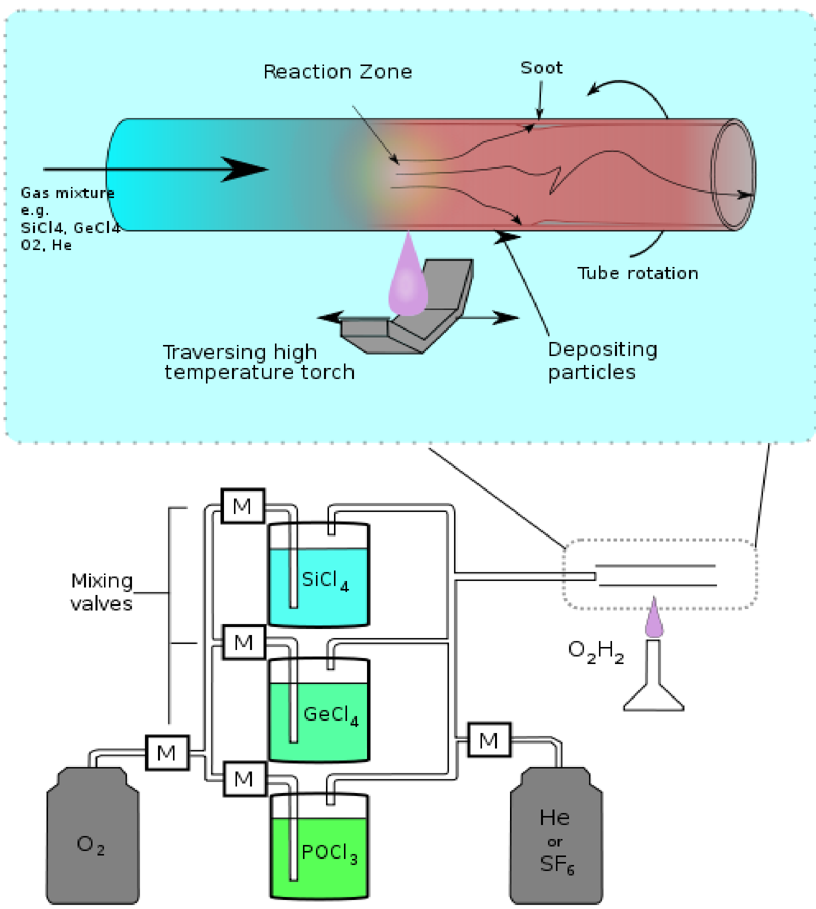


Illustration of the modified chemical vapor deposition (inside) process

Standard optical fibers are made by first constructing a large-diameter *preform*, with a carefully controlled refractive index profile, and then *pulling* the preform to form the long, thin optical fiber. The preform is commonly made by three chemical vapor deposition methods: *inside vapor deposition*, *outside vapor deposition*, and *vapor axial deposition*.

With *inside vapor deposition*, the preform starts as a hollow glass tube approximately 40 centimeters (16 in) long, which is placed horizontally and rotated slowly on a lathe. Gases such as silicon tetrachloride ($SiCl_4$) or germanium tetrachloride ($GeCl_4$) are injected with oxygen in the end of the tube. The gases are then heated by means of an external hydrogen burner, bringing the temperature of the gas up to 1900 K (1600 °C, 3000 °F), where the tetrachlorides react with oxygen to produce silica or germania (germanium dioxide) particles. When the reaction conditions are chosen to allow this reaction to occur in the gas phase throughout the tube volume, in contrast to earlier techniques where the reaction occurred only on the glass surface, this technique is called *modified chemical vapor deposition (MCVD)*.

The oxide particles then agglomerate to form large particle chains, which subsequently deposit on the walls of the tube as soot. The deposition is due to the large difference in temperature between the gas core and the wall causing the gas to push the particles outwards (this is known as thermophoresis). The torch is then traversed up and down the length of the tube to deposit the material evenly. After the torch has reached the end of the tube, it is then brought back to the beginning of the tube and the deposited particles are then melted to form a solid layer. This process is repeated until a sufficient amount of material has been deposited. For each layer the composition can be modified by varying the gas composition, resulting in precise control of the finished fiber's optical properties.

In outside vapor deposition or vapor axial deposition, the glass is formed by *flame hydrolysis*, a reaction in which silicon tetrachloride and germanium tetrachloride are oxidized by reaction with water (H_2O) in an oxyhydrogen flame. In outside vapor deposition the glass is deposited onto a solid rod, which is removed before further processing. In vapor axial deposition, a short *seed rod* is used, and a porous preform, whose length is not limited by the size of the source rod, is built up on its end. The porous preform is consolidated into a transparent, solid preform by heating to about 1800 K (1500 °C, 2800 °F).

The preform, however constructed, is then placed in a device known as a drawing tower, where the preform tip is heated and the optic fiber is pulled out as a string. By measuring the resultant fiber width, the tension on the fiber can be controlled to maintain the fiber thickness.

Coatings

The light is "guided" down the core of the fiber by an optical "cladding" with a lower refractive index that traps light in the core through "total internal reflection."

The cladding is coated by a "buffer" that protects it from moisture and physical damage. The buffer is what gets stripped off the fiber for termination or splicing. These coatings are UV-cured urethane acrylate composite materials applied to the outside of the fiber during the drawing process. The coatings protect the very delicate strands of glass fiber—about the size of a human hair—and allow it to survive the rigors of manufacturing, proof testing, cabling and installation.

Today's glass optical fiber draw processes employ a dual-layer coating approach. An inner primary coating is designed to act as a shock absorber to minimize attenuation caused by microbending. An outer secondary coating protects the primary coating against mechanical damage and acts as a barrier to lateral forces. Sometimes a metallic armour layer is added to provide extra protection.

These fiber optic coating layers are applied during the fiber draw, at speeds approaching 100 kilometers per hour (60 mph). Fiber optic coatings are applied using one of two methods: wet-on-dry, in which the fiber passes through a primary coating application, which is then UV cured, then through the secondary coating application which is subsequently cured; and wet-on-wet, in which the fiber passes through both the primary and secondary coating applications and then goes to UV curing.

Fiber optic coatings are applied in concentric layers to prevent damage to the fiber during the drawing application and to maximize fiber strength and microbend resistance. Unevenly coated fiber will experience non-uniform forces when the coating expands or contracts, and is susceptible to greater signal attenuation. Under proper drawing and coating processes, the coatings are concentric around the fiber, continuous over the length of the application and have constant thickness.

Fiber optic coatings protect the glass fibers from scratches that could lead to strength degradation. The combination of moisture and scratches accelerates the aging and deterioration of fiber strength. When fiber is subjected to low stresses over a long period, fiber fatigue can occur. Over time or in extreme conditions, these factors combine to cause microscopic flaws in the glass fiber to propagate, which can ultimately result in fiber failure.

Three key characteristics of fiber optic waveguides can be affected by environmental conditions: strength, attenuation and resistance to losses caused by microbending. External fiber optic coatings protect glass optical fiber from environmental conditions that can affect the fiber's performance and long-term durability. On the inside, coatings ensure the reliability of the signal being carried and help minimize attenuation due to microbending.

Practical issues

Optical fiber cables

An optical fiber cable

In practical fibers, the cladding is usually coated with a tough resin *buffer* layer, which may be further surrounded by a *jacket* layer, usually glass. These layers add strength to the fiber but do not contribute to its optical wave guide properties. Rigid fiber assemblies sometimes put light-absorbing ("dark") glass between the fibers, to prevent light that leaks out of one fiber from entering another. This reduces cross-talk between the fibers, or reduces flare in fiber bundle imaging applications.

Modern cables come in a wide variety of sheathings and armor, designed for applications such as direct burial in trenches, high voltage isolation, dual use as power lines, installation in conduit, lashing to aerial telephone poles, submarine installation, and insertion in paved streets. The cost of small fiber-count pole-mounted cables has greatly decreased due to the high demand for fiber to the home (FTTH) installations in Japan and South Korea.

Fiber cable can be very flexible, but traditional fiber's loss increases greatly if the fiber is bent with a radius smaller than around 30 mm. This creates a problem when the cable is bent around corners or wound around a spool, making FTTX installations more complicated. "Bendable fibers", targeted towards easier installation in home environments, have been standardized as ITU-T G.657. This type of fiber can be bent with a radius as low as 7.5 mm without adverse impact. Even more bendable fibers have been developed. Bendable fiber may also be resistant to fiber hacking, in which the signal in a fiber is surreptitiously monitored by bending the fiber and detecting the leakage.

Another important feature of cable is cable withstanding against the horizontally applied force. It is technically called max tensile strength defining how much force can applied to the cable during the installation period.

Telecom Anatolia fiber optic cable versions are reinforced with aramid yarns or glass yarns as intermediary strength member. In commercial terms, usage of the glass yarns are more cost effective while no loss in mechanical durability of the cable. Glass yarns also protect the cable core against rodents and termites.

Termination and splicing

ST connectors on multi-mode fiber

Optical fibers are connected to terminal equipment by optical fiber connectors. These connectors are usually of a standard type such as *FC*, *SC*, *ST*, *LC*, or *MTRJ*.

Optical fibers may be connected to each other by connectors or by *splicing*, that is, joining two fibers together to form a continuous optical waveguide. The generally accepted splicing method is arc fusion splicing, which melts the fiber ends together with an electric arc. For quicker fastening jobs, a "mechanical splice" is used.

Fusion splicing is done with a specialized instrument that typically operates as follows: The two cable ends are fastened inside a splice enclosure that will protect the splices, and the fiber ends are stripped of their protective polymer coating (as well as the more sturdy outer jacket, if present). The ends are *cleaved* (cut) with a precision cleaver to make them perpendicular, and are placed into special holders in the splicer. The splice is usually inspected via a magnified viewing screen to check the cleaves before and after the splice. The splicer uses small motors to align the end faces together, and emits a small spark between electrodes at the gap to burn off dust and moisture. Then the splicer generates a larger spark that raises the temperature above the melting point of the glass, fusing the ends together permanently. The location and energy of the spark is carefully controlled so that the molten core and cladding do not mix, and this minimizes optical loss. A splice loss estimate is measured by the splicer, by directing light through the cladding on one side and measuring the light leaking from the cladding on the other side. A splice loss under 0.1 dB is typical. The complexity of this process makes fiber splicing much more difficult than splicing copper wire.

Mechanical fiber splices are designed to be quicker and easier to install, but there is still the need for stripping, careful cleaning and precision cleaving. The fiber ends are aligned and held together by a precision-made sleeve, often using a clear index-matching gel that enhances the transmission of light across the joint. Such joints typically have higher optical loss and are less robust than fusion splices, especially if the gel is used. All splicing techniques involve the use of an enclosure into which the splice is placed for protection afterward.

Fibers are terminated in connectors so that the fiber end is held at the end face precisely and securely. A fiber-optic connector is basically a rigid cylindrical barrel surrounded by a sleeve that holds the barrel in its mating socket. The mating mechanism can be "push and click", "turn and latch" ("bayonet"), or screw-in (threaded). A typical connector is installed by preparing the fiber end and inserting it into the rear of the connector body. Quick-set adhesive is usually used so the fiber is held securely, and a strain relief is secured to the rear. Once the adhesive has set, the fiber's end is polished to a mirror finish. Various polish profiles are used, depending on the type of fiber and the application. For single-mode fiber, the fiber ends are typically polished with a slight curvature, such that when the connectors are mated the fibers touch only at their cores. This is known as a "physical contact" (PC) polish. The curved surface may be polished at an angle, to make an "angled physical contact" (APC) connection. Such connections have higher loss than PC connections, but greatly reduced back reflection, because light that reflects from the angled surface leaks out of the fiber core; the resulting loss in signal strength is known as gap loss. APC fiber ends have low back reflection even when disconnected.

In the 1990s, terminating fiber optic cables was very labor intensive. The number of parts per connector, polishing of the fibers, and the need to oven-bake the epoxy in each connector made terminating fiber optic cables very difficult. Today, many different connectors are on the market and offer an easier, less labor intensive way of terminating the cables. Some of the most popular connectors have already been polished from the factory and include a gel inside the connector and those two steps help save money on labor especially on large projects. A cleave is made at a required length in order to get as close to the polished piece already inside the connector, with the gel surrounding the point where the two piece meet inside the connector very little light loss is exposed.

Free-space coupling

It is often necessary to align an optical fiber with another optical fiber, or with an optoelectronic device such as a light-emitting diode, a laser diode, or a modulator. This can involve either carefully aligning the fiber and placing it in contact with the device, or can use a lens to allow coupling over an air gap. In some cases the end of the fiber is polished into a curved form that is designed to allow it to act as a lens.

In a laboratory environment, a bare fiber end is coupled using a fiber launch system, which uses a microscope objective lens to focus the light down to a fine point. A precision translation stage (micro-positioning table) is used to move the lens, fiber, or device to allow the coupling efficiency to be optimized. Fibers with a connector on the end make this process much simpler: the connector is simply plugged into a pre-aligned fiberoptic collimator, which contains a lens that is either accurately positioned with respect to the fiber, or is adjustable. To achieve the best injection efficiency into single-mode fiber, the direction, position, size and divergence of the beam must all be optimized. With good beams, 70 to 90% coupling efficiency can be achieved.

With properly polished single-mode fibers, the emitted beam has an almost perfect Gaussian shape—even in the far field—if a good lens is used. The lens needs to be large enough to support the full numerical aperture of the fiber, and must not introduce aberrations in the beam. Aspheric lenses are typically used.

Fiber fuse

At high optical intensities, above 2 megawatts per square centimeter, when a fiber is subjected to a shock or is otherwise suddenly damaged, a *fiber fuse* can occur. The reflection from the damage vaporizes the fiber immediately before the break, and this new defect remains reflective so that the damage propagates back toward the transmitter at 1–3 meters per second (4−11 km/h, 2–8 mph). The open fiber control system, which ensures laser eye safety in the event of a broken fiber, can also effectively halt propagation of the fiber fuse. In situations, such as undersea cables, where high power levels might be used without the need for open fiber control, a "fiber fuse" protection device at the transmitter can break the circuit to prevent any damage.

Example

Fiber connections can be used for various types of connections. For example, most high definition televisions offer a digital audio optical connection. This allows the streaming of audio over light, using the TOSLink protocol.

Electric power transmission

Optical fiber can be used to transmit electricity. While the efficiency is not nearly that of traditional copper wire, it is especially useful in situations where it is desirable to not have a metallic conductor as in the case of use near MRI machines which produce strong magnetic currents.