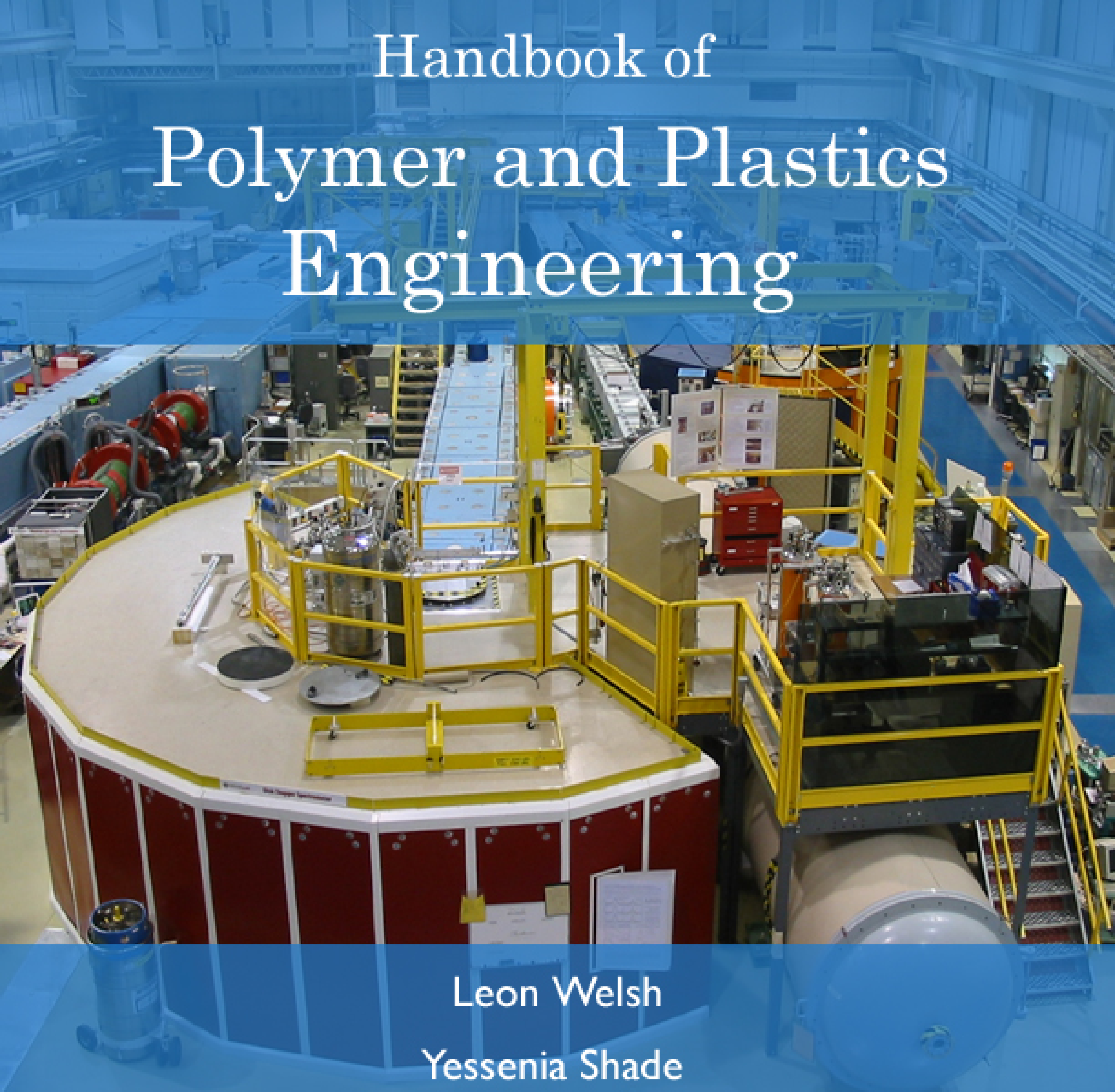
Handbook of Polymer and Plastics Engineering



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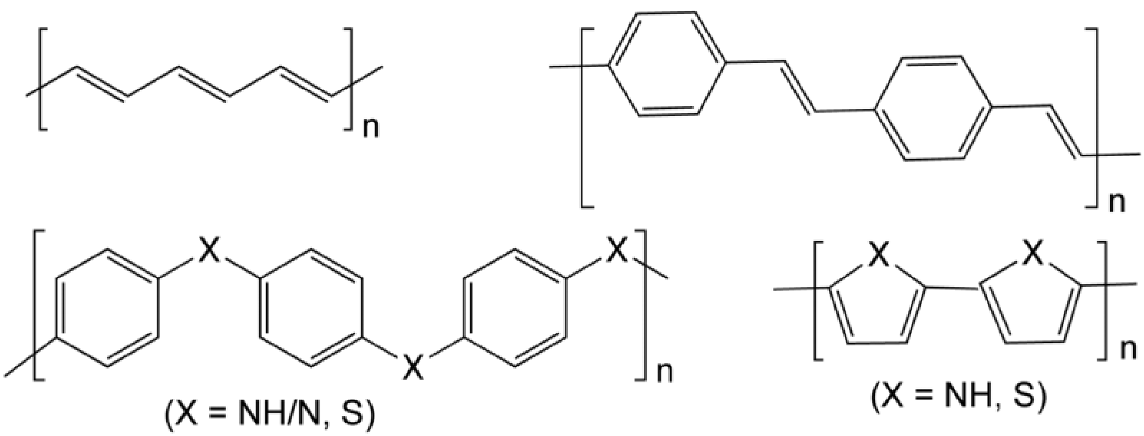
Chapter 1

Conductive Polymer



Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).

Conductive polymers or, more precisely, **intrinsically conducting polymers** (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not plastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Types

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Historically, these are known as melanins. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

The following table presents some organic conductive polymers according to their composition. **The well-studied classes are written in bold** and *the less well studied ones are in italic*.

The main chain contains		Heteroatoms present	
	No heteroatom	**Nitrogen-containing**	**Sulfur-containing**
Aromatic cycles	• *Poly(fluorene)s* • *polyphenylenes* • *polypyrenes* • *polyazulenes* • *polynaphthalenes*	The N is in the aromatic cycle: • **poly(pyrrole)s (PPY)** • *polycarbazoles* • *polyindoles* • *polyazepines* The N is outside the aromatic cycle: • **polyanilines (PANI)**	The S is in the aromatic cycle: • **poly(thiophene)s (PT)** • **poly(3,4-ethylenedioxythiophene) (PEDOT)** The S is outside the aromatic cycle: • **poly(p-phenylene sulfide) (PPS)**
Double bonds	• **Poly(acetylene)s (PAC)**		
Aromatic cycles and double bonds	• **Poly(p-phenylene vinylene) (PPV)**		

Synthesis

There are many methods for the synthesis of conductive polymers. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation:

$$n\ H–[X]–H \rightarrow H–[X]_n–H + 2(n–1)\ H^+ + 2(n–1)\ e^-$$

The low solubility of most polymers presents challenges. Some researchers have addressed this through the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water. These include polyaniline nanofibers and PEDOT:PSS. These materials have lower molecular weights than that of some materials previously explored in the literature. However, in some cases, the molecular weight need not be high to achieve the desired properties.

Molecular basis of electrical conductivity

The conductivity of such polymers is the result of several processes. E.g., in traditional polymers such as polyethylenes, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich (e.g., phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

The most notable difference between conductive polymers and inorganic semiconductors is the electron mobility, which until very recently was dramatically lower in conductive polymers than their inorganic counterparts. This difference is diminishing with the invention of new polymers and the development of new processing techniques. Low charge carrier mobility is related to structural disorder. In fact, as with inorganic amorphous semiconductors, conduction in such relatively disordered materials is mostly a function of "mobility gaps" with phonon-assisted hopping, polaron-assisted tunneling, etc., between localized states. Recently, it has been reported that Quantum Decoherence on localized electron states might be the fundamental mechanism behind electron transport in conductive polymers.

The conjugated polymers in their undoped, pristine state are semiconductors or insulators. As such, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is poorly understood yet. Generally it is assumed, that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however, this could not be confirmed for PEDOT and polyaniline which are largely amorphous.

Properties and applications

Conductive polymers enjoy few large-scale applications due to their poor processability. They have been known to have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, provide fresh air to this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

Electroluminescence

Electroluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Barriers to applications

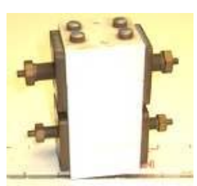
Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can processed only by dispersion.

Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. To date, there remains to be discovered an organic polymer that is *intrinsically* electrically conducting.

History



voltage-controlled switch, an organic polymer electronic device from 1974. Now in the Smithsonian Chips collection.

There are multiple reviews of the history of the field. The first report on polyaniline goes back to the discovery of aniline. In the mid-19th century, Letheby reported the electrochemical and chemical oxidation products of aniline in acidic media, noting that reduced form was colourless but the oxidized forms were deep blue. In the early 20th century, German chemists named several compounds "aniline black" and "pyrrole black" and used them industrially. Classically, such polymer "blacks", their parent compound polyacetylene, and their co-polymers were called "Melanins".

The first highly-conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. In 1954, researchers at Bell Labs and elsewhere reported organic charge transfer complexes with resistivities as low as 8 ohms-cm. In the early 1970s, salts of tetrathiafulvalene were shown to exhibit almost metallic conductivity, while superconductivity was demonstrated in 1980. Broad research on charge transfer salts continues today. While these compounds were technically not polymers, this indicated that organic compounds can carry current. While organic conductors were previously intermittently discussed, the field was particularly energized by the prediction of superconductivity following the discovery of BCS theory.

In 1963 Australians Bolto, DE Weiss, and coworkers reported iodine-doped oxidized polypyrrole blacks with resistivities as low as 1 ohm/cm. This Australian group eventually claimed to reach resistivities as low as 0.03 ohm·cm with other conductive organic polymers. This resistivity is roughly equivalent to present-day efforts. The 1964 monograph *Organic Semiconductors* cites multiple reports of similar high-conductivity oxidized polyacetylenes. With the notable exception of Charge transfer complexes (some of which are even superconductors), organic molecules were previously considered insulators or at best weakly conducting semiconductors. Subsequently, DeSurville and coworkers reported high conductivity in a polyaniline. Likewise, in 1980, Diaz and Logan reported films of polyaniline that can serve as electrodes.

Similarly, much early work on the physics and chemistry of conductive polymers was done under the melanin rubrick. This was because of the medical relevance of this material. For example, in the 1960s Blois *et al.* showed semiconduction in melanins, as well as further defining their physical structures and properties Nicolaus *et al.* further defined the conductive polymer structures. Classically, all polyacetylenes, polypyrroles and polyanilines are melanins, "The most simple melanin can be considered the acetylene-black from which it is possible to derive all the others.. Substitution does not qualitatively influence the physical properties like conductivity, colour, EPR, which remain unaltered."

However, while mostly operating in the quantum realm of less than 100 nanometers, "molecular" electronic processes can collectively manifest on a macro scale. Examples include quantum tunneling, negative resistance, phonon-assisted hopping, polarons, and the like. Thus, macro-scale active organic electronic devices were described decades before molecular-scale ones. E.g., in 1974, John McGinness and his coworkers described the putative "first experimental demonstration of an operating molecular electronic device". This was an "active" organic-polymer electronic device, a voltage-controlled bistable switch. As its active element, this device used DOPA-melanin, a well-characterized self-doping copolymer of polyaniline, polypyrrole, and polyacetylene. The "ON" state of this device exhibited almost metallic conductivity, and exhibited low conductivity with switching, with as much as five orders of magnitude shifts in current. Their material also exhibited classic negative differential resistance.

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. This research earned them the 2000 Nobel prize in Chemistry *"For the discovery and development of conductive polymers."* The Nobel citation made no reference to Weiss *et al.'s* similar earlier work. Because of the numerous earlier reports of similar compounds, reviewers question the Nobel citation's *discovery* assignment. Thus, Inzelt notes that, while the Nobelists deserve credit for publicising and popularizing the field, conductive polymers were " *..produced, studied and even applied* " well before their work.

Chapter 2

Coordination Polymers

Coordination polymers are inorganic structures containing metal cation centers linked by ligands, extending in an array. They can also be described as polymers whose repeat units are coordination complexes. Similar supramolecular architectures are also called Metal-organic frameworks (MOFs), and coordination networks, with some inconsistency in the distinctions between the terms. (An IUPAC project was initiated in 2009 to address the terminology issues in this area and will deliver its final report in 2011.) Coordination polymers span scientific fields such as organic and inorganic chemistry, biology, materials science, electrochemistry, and pharmacology, having many potential applications. This interdisciplinary nature has led to extensive study in the past few decades.

Coordination polymers can be classified in a number of different ways due to particular aspects of structure and composition. One important classification is referred to as dimensionality. A structure can be determined to be one, two or three dimensional, depending on the number of directions in space the array extends in. A one dimensional structure extends in a straight line (along the x axis); a two dimensional structure extends in a plane (two directions, x and y axes); and a three dimensional structure extends in all three directions (x, y, and z axes). This is depicted in Figure 1.

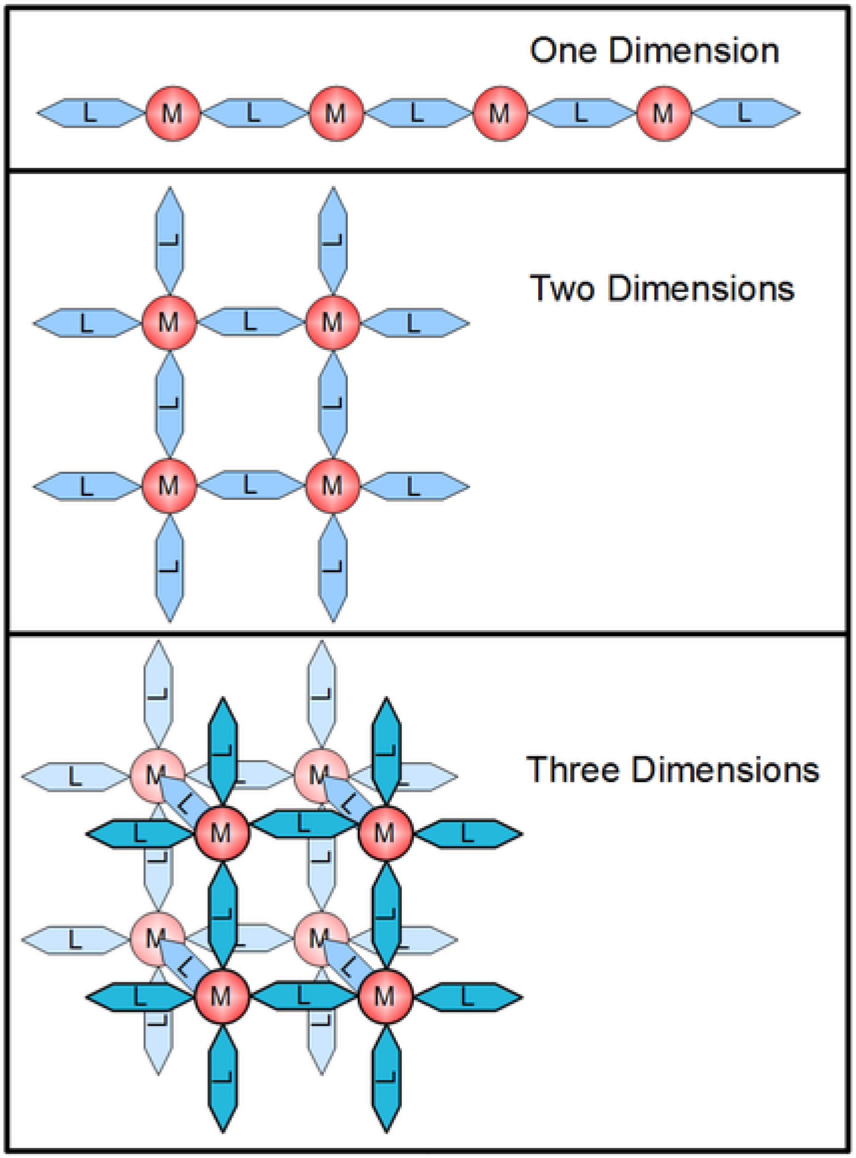


Figure 1. An illustration of 1- 2- and 3-dimensionality.

History

Even though coordination polymers have experienced a research boom in the past decade or so, research in this field has been around for a long time. Alfred Werner, sometimes called the father of coordination chemistry, won the Nobel Prize for Chemistry in 1913 "for his work on the linkage of atoms in molecules, by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry." This work laid a lot of the groundwork for the future study of coordination polymers. Terms ubiquitous in the field, such as coordination number, were coined by Werner. He also determined that even neutral, stable molecules in their own right (such as ammonia or water) can behave like ligands, and enter into coordination bonds with metals.

In the past few decades, research in this field has boomed, partially because of the potential applications for metal-organic frameworks (MOF's) in areas such as hydrogen storage.

Synthesis and Propagation

Much of the mechanism for growth coordination polymers is based on self-assembly, involving crystallization of a metal salt with a ligand. This can be achieved by known crystallization and crystal engineering techniques. The mechanisms of Molecular self-assembly processes on a molecular level are currently being investigated, however it is accepted that coordination generally emerges due to the interaction of lone pairs of electrons on the ligand with the regions of low electron density on the cationic metal ion. Crystals of coordination polymers are nucleated when an aggregate of coordinated ligand/metal complexes reaches a size where lowered energy of the aggregate as a whole is more significant than the added surface energy. This means that the crystal will grow more easily in terms of energy as opposed to de-aggregation. This phenomenon is known as nucleation. The nucleus is a localized, thermodynamic site for crystal growth to occur. More molecules (metals and ligands) can self-assemble onto the growing crystal in a periodic array.

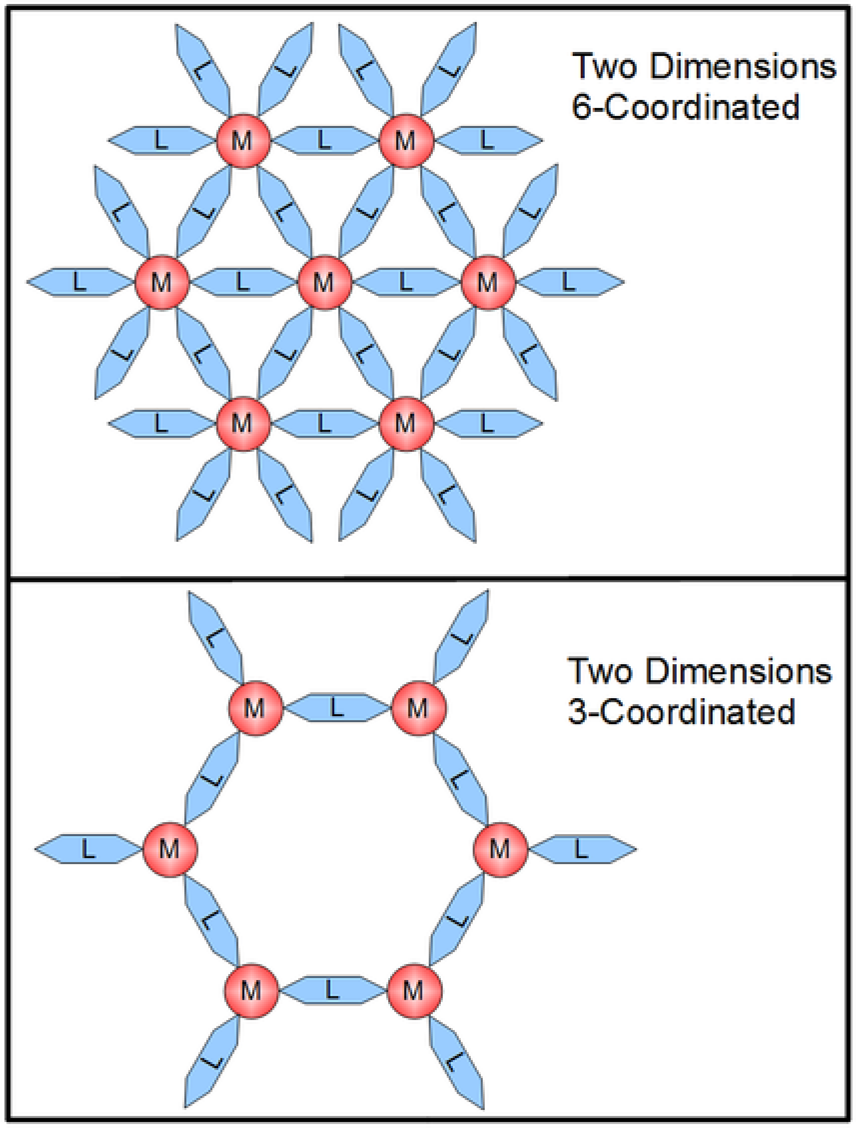


Figure 2. Shows planar geometries with 3 coordination and 6 coordination.

For the most part, it is not possible right now to draw any direct correlations between particular structural aspects and applications.

The synthesis methods utilized to produce coordination polymers are generally the same methods used to grow any crystal. These generally include solvent layering (slow diffusion), slow evaporation, and slow cooling. (Because the main method of characterization of coordination polymers is X-ray crystallography, growing a crystal of sufficient size and quality is important.)

Intermolecular Forces and Bonding

The forces that led to spontaneous arrangement of molecules (metal-ligand complexes in this case) are thought to be van der Waals forces, pi-pi interactions, hydrogen bonding, and stabilization of pi bonds by polarized bonds in addition to the coordination bond formed between the metal and the ligand. These intermolecular forces tend to be weak, with a long equilibrium distance (bond length) compared to covalent bonds. The pi-pi interactions between benzene rings, for example, have energy roughly 5-10 kJ/mol and optimum spacing 3.4-3.8 Ångstroms between parallel faces of the rings.

Coordination

The crystal structure and dimensionality of the coordination polymer is determined by the functionality of the linker and the coordination geometry of the metal center. Dimensionality is generally driven by the metal center which can have the ability to bond to as 16 functional sites on linkers. This number of possible bonds is the coordination number. Coordination numbers are more often between 2 and 10, and the bonding sites are separated by distinct angles. Coordination numbers are shown in planer geometry in Figure 2. In Figure 1 the 1D structure is 2-coordinated, the planer is 4-coordinated, and the 3D is 6-coordinated. Figure 3 shows structures hinting at the complexity that is possible by changing coordination geometry.

Metal Centers

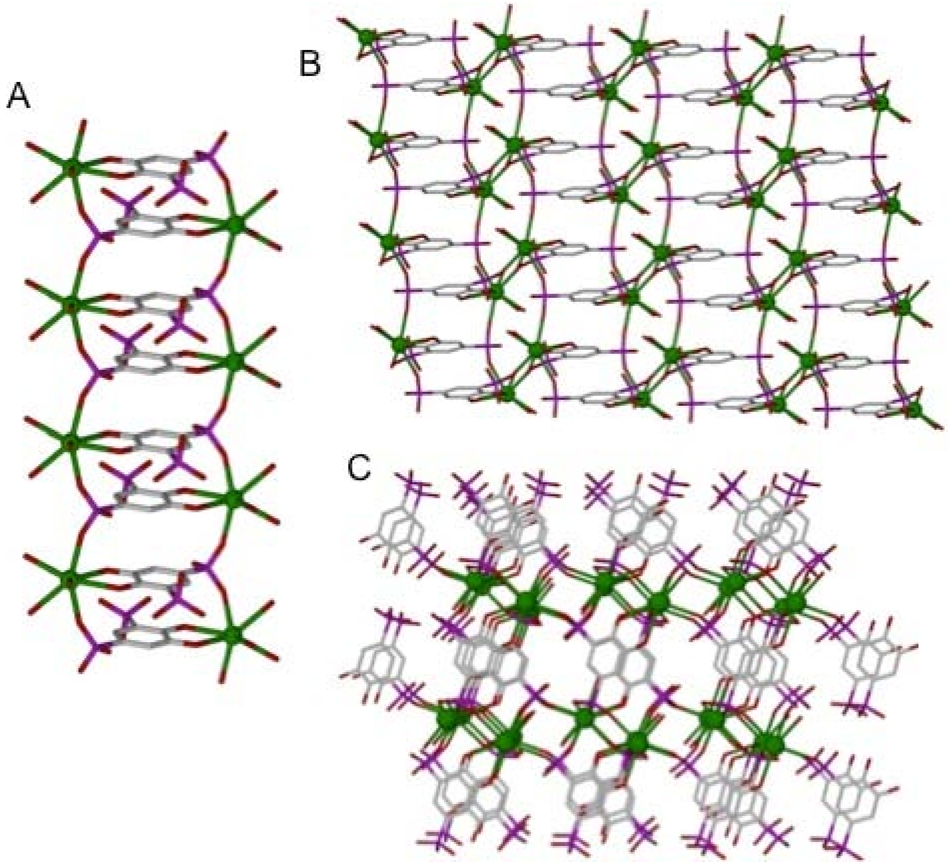


Figure 3. Shown here are three coordination polymers of different dimensionality. All three were made using the same ligand (4,5-dihydroxybenzene-1,3-disulfonate (L)), but different metal cations. All of the metals come from Group 2 on the periodic table (alkaline earth metals) and in this case, dimensionality increases with cation size and polarizability. A. $[Ca(L)(H_2O)_4]•H_2O$ B. $[Sr(L)(H_2O)4]•H_2O$ C.$[Ba(L)(H_2O)]•H_2O$ In each case, the metal is represented in green.

Metal Centers, also called nodes or hubs, bond to a specific number of linkers at well defined angles. The number of linkers bound to a node is known as the coordination number, which, along with the angles they are held at, determines the dimensionality of the structure. The coordination number and coordination geometry of a metal center is determined by the nonuniform distribution of electron density around it, and in general the coordination number increases with cation size. Several models, most notably hybridization model and molecular orbital theory, use the Schrödinger equation to predict and explain coordination geometry, however this is difficult in part because of the complex effect of environment on electron density distribution.

Transition Metals

Transition metals are commonly used as nodes. Partially filled d orbitals, either in the atom or ion, can hybridize differently depending on environment. This electronic structure causes some of them to exhibit multiple coordination geometrys, particularly copper and gold ions which as neutral atoms have full d-orbitals in their outer shells.

Lanthanides

Lanthanides are large atoms with coordination numbers varying from 7 to 10 due to filling of f orbitals. They are strongly affected by their environment and difficult to predict, making them challenging to use as nodes. This challenge may be worth it however, because the bonds formed by multiplexing(attaching to multiple linkers) have characteristic luminescent wavelengths.

Alkali/Alkaline Earth Metals

Alkali metals and alkaline earth metals exist as stable cations. Alkali metals readily form cations with stable valence shells, giving them different coordination behavior than lanthanides and transition metals. They are strongly effected by the counter ion from the salt used in synthesis, which is difficult to avoid. The coordination polymers shown in Figure 3 are all group two metals. In this case, the dimensionality of the of these structures increases as the radius of the metal increases down the group (from calcium to strontium to barium).

Ligands

In most coordination polymers, a ligand (atom or group of atoms) will formally donate a lone pair of electrons to a metal cation and form a coordination complex via a Lewis acid/ base relationship (lewis acids and bases). Coordination polymers are formed when a ligand has the ability to form multiple coordination bonds and act as a bridge between multiple metal centers. Ligands that can form one coordination bond are referred to as monodentate, but those which form multiple coordination bonds, which could lead to coordination polymers are called polydentate. Polydentate ligands are particularly important because it is through ligands that connect multiple metal centers together that an infinite array is formed. Polydentate ligands can also form multiple bonds to the same metal (which is called chelation). Monodentate ligands are also referred to as terminal because they do not offer a place for the network to continue. Often, coordination polymers will consist of a combination of poly- and monodentate, bridging, chelating, and terminal ligands.

Chemical Composition

Almost any type of atom with a lone pair of electrons can be incorporated into a ligand. Ligands that are commonly found in coordination polymers include polypyridines, phenanthrolines, hydroxyquinolines and polycarboxylates. Oxygen and nitrogen atoms are commonly encountered as binding sites, but other atoms, such as sulfur and phosphorus, have been observed.

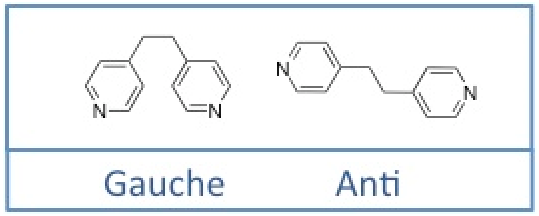


Figure 4. A flexible ligand in both a gauche and anti conformation.

Ligands and metal cations tend to follow hard soft acid base theory (HSAB) trends. This means that larger, more polarizable soft metals will coordinate more readily with larger more polarizable soft ligands, and small, non-polarizable, hard metals coordinate to small, non-polarizable, hard ligands.

Structural Orientation

Ligands can be flexible or rigid. A rigid ligand is one that has no freedom to rotate around bonds or reorient within a structure. Flexible ligands can bend, rotate around bonds, and reorient themselves. This creates more variety in the structure. There are examples of coordination polymers that include two configurations of the same ligand within one structure, as well as two separate structures where the only difference between them is ligand orientation. An example of a flexible ligand is shown in Figure 4.

Other Factors

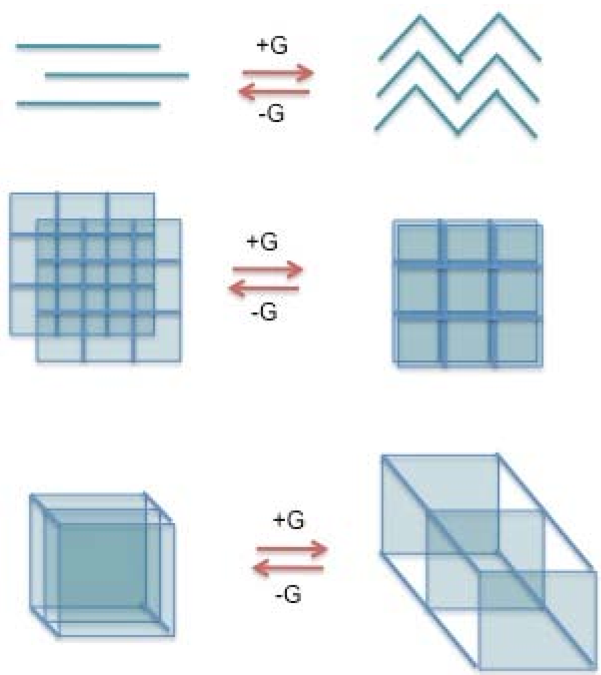


Figure6. The addition and removal of guest molecules can have a large effect on the resulting structure of a coordination polymer. A few examples are (top) change of a linear

1D chain to a zigzag pattern, (middle) staggered 2D sheets to stacked, and (bottom) 3D cubes become more widely spaced.

Counter Ion

Besides metal and ligand choice, there are many other factors that effect the structure of the coordination polymer. For example, most metal centers are positively charged ions which exist as salts. The counter ion in the salt can effect the overall structure. For example, silver salts such as $AgNO_3$, $AgBF_4$, $AgClO_4$, $AgPF_6$, $AgAsF_6$ and AgSbF are all crystallized with the same ligand, the structures vary in terms of the coordination environment of the metal, as well as the dimensionality of the entire coordination polymer.

Crystallization Environment

Additionally, variations in the crystallization environment can also change the structure. Changes in pH, exposure to light, or changes in temperature can all change the resulting structure. Influences on the structure based on changes in crystallization environment are determined on a case by case basis.

Guest Molecules

The structure of coordination polymers oftentimes incorporates empty space in the form of pores or channels. This empty space is thermodynamically unfavorable. In order to stabilize the structure and prevent collapse, the pores or channels are often occupied by guest molecules. Guest molecules do not form bonds with the surrounding lattice, but sometimes interact via intermolecular forces, such as hydrogen bonding or pi stacking. Most often, the guest molecule will be the solvent that the coordination polymer was crystallized in, but can really be anything (other salts present, atmospheric gases such as oxygen, nitrogen, carbon dioxide, etc.) The presence of the guest molecule can sometimes influence the structure by supporting a pore or channel, where otherwise none would exist. Figure 5 shows a schematic of a few different ways a structure can change upon the addition or evacuation of a guest molecule.

Applications

Molecular Storage

Thanks to coordination polymerization in three dimensions, pores within the structure can be made. The size and shapes of the pore can be controlled by the linker size and the connecting ligands' length and functional groups. To modify the pore size in order to achieve effective adsorption, nonvolatile guests (host-guest chemistry) are intercalated in the porous coordination polymer space to decrease the pore size. Active surface guests can also be used contribute to adsorption. For example, the large-pore MOF-177, 11.8 Å in diameter, can be doped by C_{60} molecules (6.83 Å in diameter) or polymers with a highly conjugated system in order to increase the surface area for H_2 adsorption. Flexible porous coordination polymers are also convenient for molecular storage, since their pore sizes can be easily altered by physical changes. And example of this might be seen in a polymer that contains gas molecules in its normal state, but upon compression the polymer collapses and releases the stored molecules. Depending on the crystal structure of the polymer, it is possible that the structure be flexible enough that collapsing the pores is reversible and the polymer can be reused to uptake the gas molecules again. The Metal-organic framework page has a detailed section dealing with H_2 gas storage.

Luminescence

Luminescence arises from electronic transitions from an excited state, caused by photoexcitation, to the ground state, resulting in the emission of light. Most luminescent compounds require organic chromophoric ligands, which absorb light and then pass the excitation energy to the metal ion, which is referred to as a ligand-to-metal charge-transfer process (LMCT). Coordination polymers are potentially the most versatile luminescent species due to their emission properties being coupled with guest exchange. Luminescent supramolecular architectures have recently attracted much interest because of their potential applications in optoelectronic devices or as fluorescent sensors and probes. Coordination polymers are often more stable (thermo- and solvent-resistant) than purely organic species. For ligands that fluoresce without the presence of the metal linker (not due to LMCT), the intense photoluminescence emission of these materials tend to be magnitudes of order higher than that or the free ligand alone. These materials can be used for designing potential candidates for light emitting diode (LED) devices. The dramatic increase in fluorescence is caused by the increase in rigidity and asymmetry of the ligand when coordinated to the metal center.

Electrical Conductivity

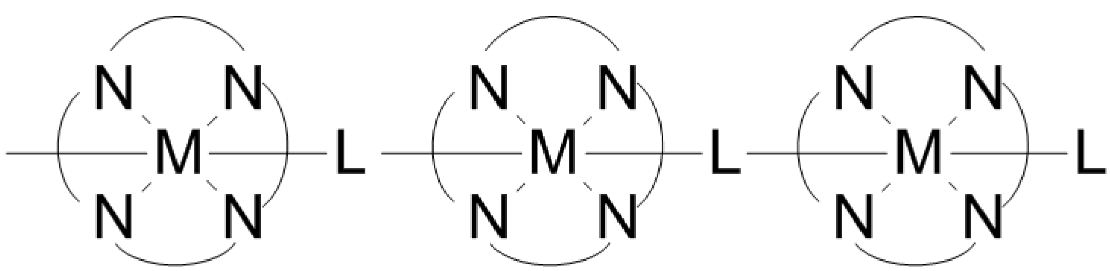


Figure 7. Structure of coordination polymers that exhibit conductivity, where M = Fe, Ru, OS; L = octaethylporphyrinato or pthalocyaninato; N belongs to pyrazine or bipyridine.

Coordination polymers can have short inorganic and conjugated organic bridges in their structures, which provide pathways for electrical conduction. Some one-dimensional coordination polymers built as shown in Fig. X exhibit conductivities in a range of $1x10^{-6}$ to $2x10^{-1}$ S/cm. The conductivity is due to the interaction between the metal d-orbital and the pi* level of the bridging ligand. In some cases coordination polymers can have semi-conductor behavior. Three-dimensional structures consisting of sheets of silver-containing polymers demonstrate semi-conductivity when the metal centers are aligned, and conduction decreases as the silver atoms go from parallel to perpendicular.

Magnetism

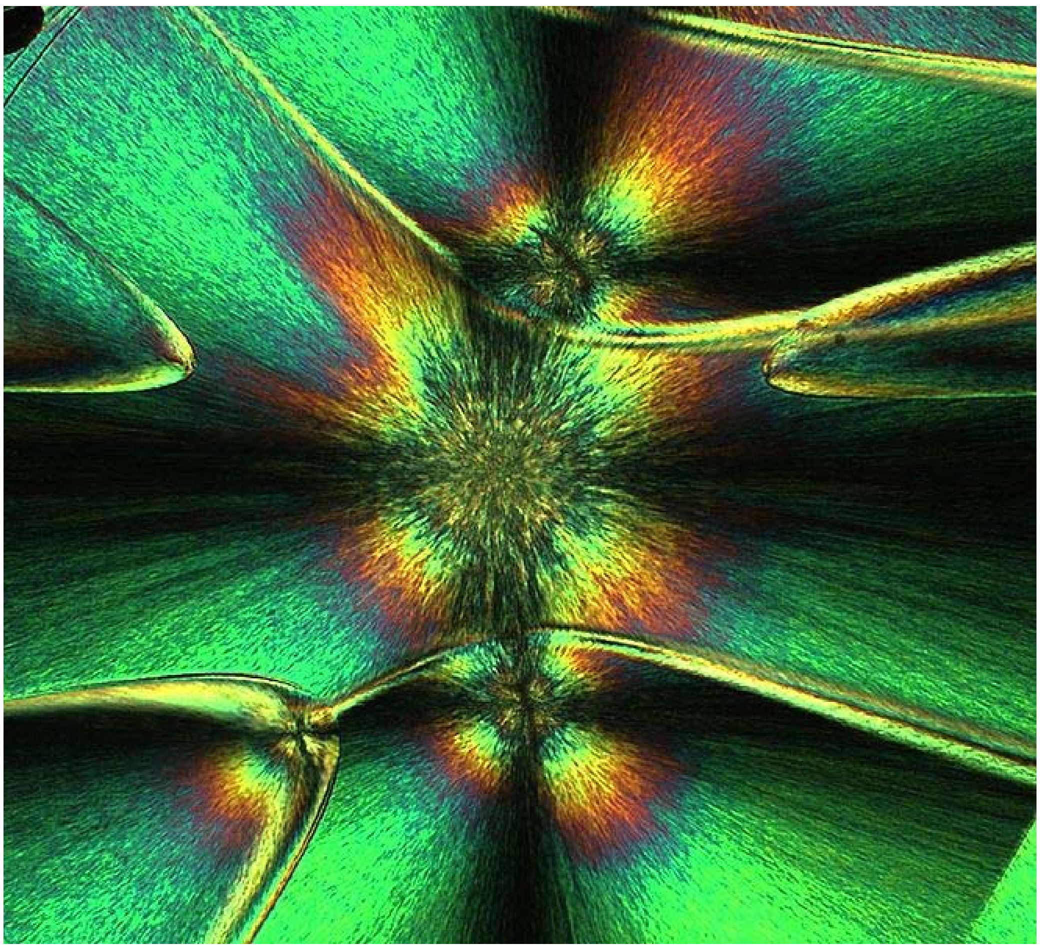
Interest in coordination polymers is continued by the application of magnetism. Antiferromagnetism, ferrimagnetism, and ferromagnetism are cooperative phenomena of the magnetic spins within a solid. They require an interaction or coupling between the spins of the paramagnetic centers. Since intramolecular interactions (such as bonding) are much more efficient than intermolecular interactions (i.e. through space), three-dimensional coordination polymers are of interest because they connect their magnetic centers through direct coordinative links, and have the possibility for displaying high critical temperatures. In order to allow efficient magnetic, metal ions should be bridged by small ligands allowing for short metal-metal contacts (such as oxo, cyano, and azido bridges).

Sensor Capability

Coordination polymers can also show color changes upon the change of solvent molecules incorporated into the structure. An example of this would be the two Co coordination polymers of the $[Re_6S_8(CN)_6]^{4-}$ cluster that contains water ligands that coordinate to the cobalt atoms. This originally orange solution turns either purple or green with the replacement of water with tetrahydrofuran, and blue upon the addition of diethyl ether. The polymer can thus act as a solvent sensor that physically changes color in the presence of certain solvents. The color changes are attributed to the incoming solvent displacing the water ligands on the cobalt atoms, resulting in a change of their geometry from octahedral to tetrahedral.

Chapter 3

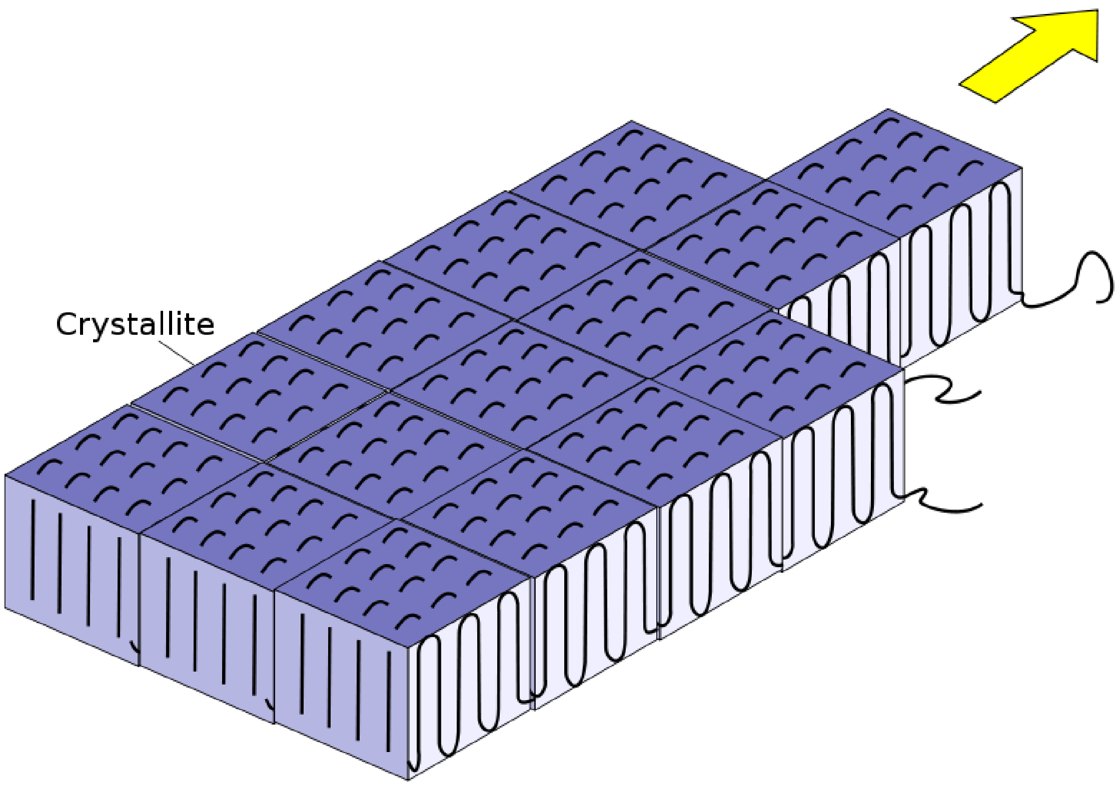
Spherulite (Polymer Physics)



Spherulites viewed between crossed polarizers in an optical microscope.

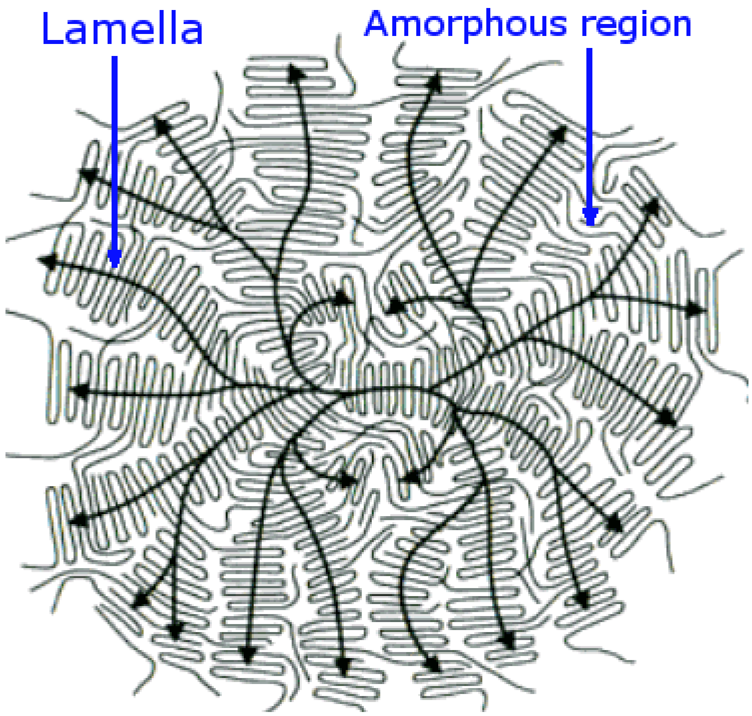
In polymer physics, **spherulites** are spherical semicrystalline regions inside non-branched linear polymers. Their formation is associated with crystallization of polymers from the melt and is controlled by several parameters such as the number of nucleation sites, structure of the polymer molecules, cooling rate, etc. Depending on those parameters, spherulite diameter may vary in a wide range from a few micrometers to millimeters. Spherulites are composed of highly ordered lamellae, which result in higher density, hardness, but also brittleness of the spherulites as compared to disordered polymer. The lamellae are connected by amorphous regions which provide certain elasticity and impact resistance. Alignment of the polymer molecules within the lamellae results in birefringence producing a variety of colored patterns, including Maltese cross, when spherulites are viewed between crossed polarizers in an optical microscope.

Formation



Principle of lamellae formation during the crystallization of polymers. Arrow shows the direction of temperature gradient.

If a molten linear polymer (such as polyethylene) is cooled down rapidly, then the orientation of its molecules, which are randomly aligned, curved and entangled remain frozen and the solid has disordered structure. However, upon slow cooling, some polymer chains take on a certain *orderly configuration*: they align themselves in plates called *crystalline lamellae*.



Schematic model of a spherulite. Black arrows indicate direction of molecular alignment

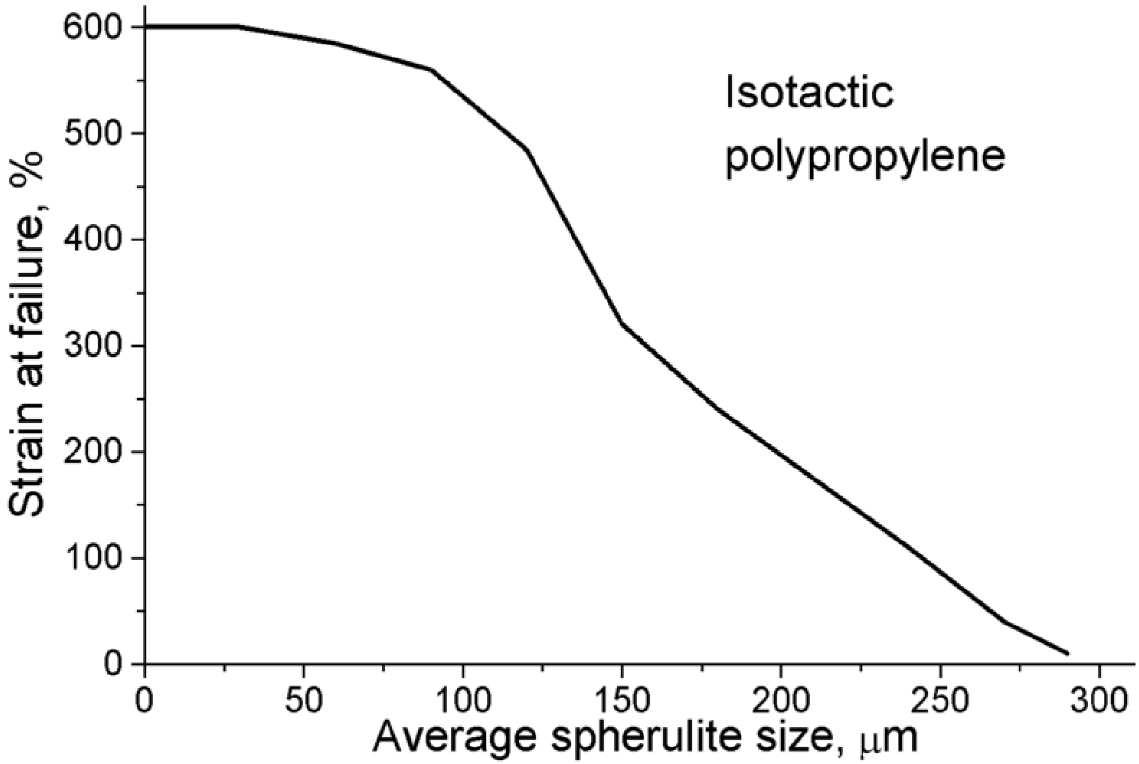
Growth from the melt would follow the temperature gradient (see figure). For example, if the gradient is directed normal to the direction of molecular alignment then the lamella growth sideward into a planar crystallite. However, in absence of thermal gradient, growth occurs radially, in all directions resulting in spherical aggregates, that is spherulites. The largest surfaces of the lamellae are terminated by molecular bends and kinks, and growth in this direction results in disordered regions. Therefore, spherulites have semicrystalline structure where highly ordered lamellae plates are interrupted by amorphous regions.

The size of spherulites varies in a wide range, from microns up to 1 centimeter and is controlled by the nucleation. Strong supercooling or intentional addition of crystallization seeds results in relatively large number of nucleation sites; then spherulites are numerous and small and interact with each other upon growth. In case of fewer nucleation sites and slow cooling, a few larger spherulites are created.

The seeds can be induced by impurities, plasticizers, fillers, dyes and other substances added to improve other properties of the polymer. This effect is poorly understood and irregular, so that the same additive can promote nucleation in one polymer, but not in another. Many of the good nucleating agents are metal salts of organic acids, which themselves are crystalline at the solidification temperature of the polymer solidification.

Properties

Mechanical

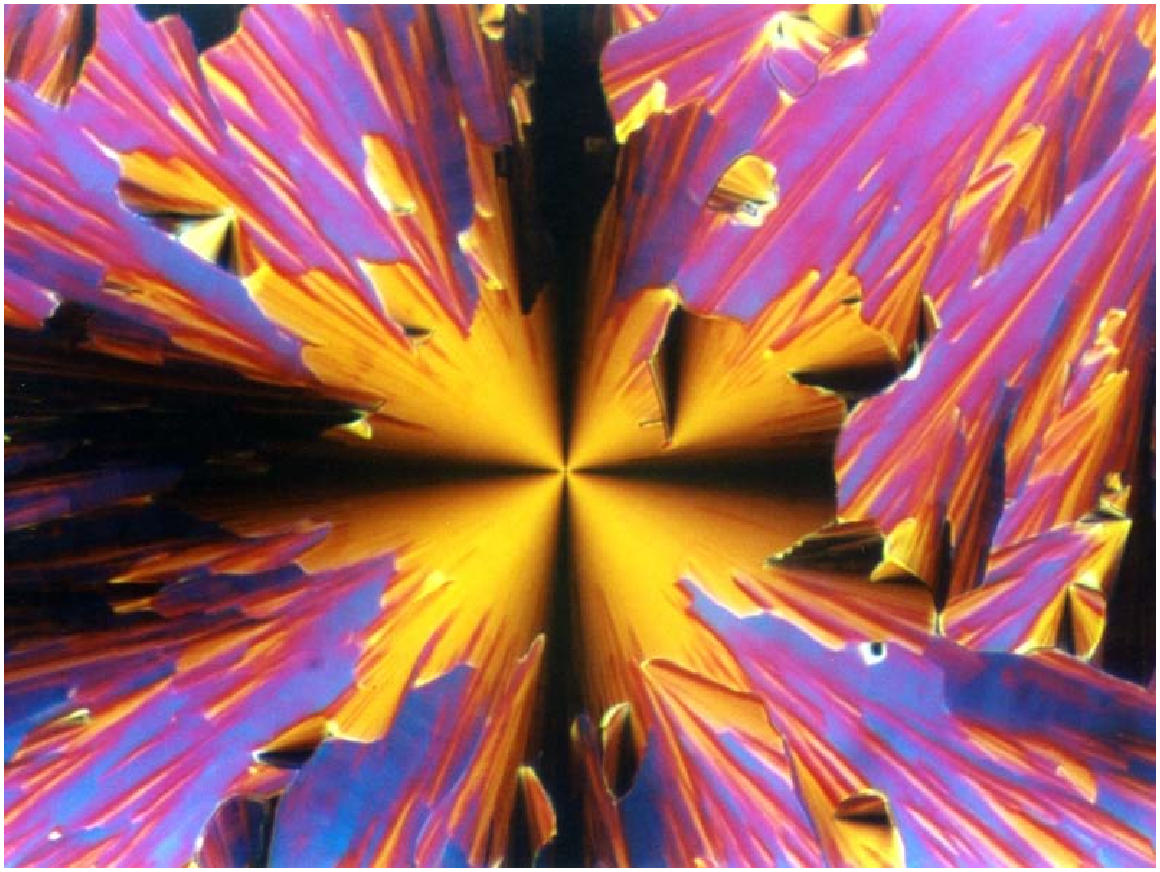


Strain at failure vs. spherulite size.

Formation of spherulites affects many properties of the polymer material; in particular, crystallinity, density, tensile strength and Young's modulus of polymers increase during spherulization. This increase is due to the lamellae fraction within the spherulites, where the molecules are more densely packed than in the amorphous phase. Stronger intermolecular interaction within the lamellae accounts for increased hardness, but also for higher brittleness. On the other hand, the amorphous regions between the lamellae within the spherulites give the material certain elasticity and impact resistance.

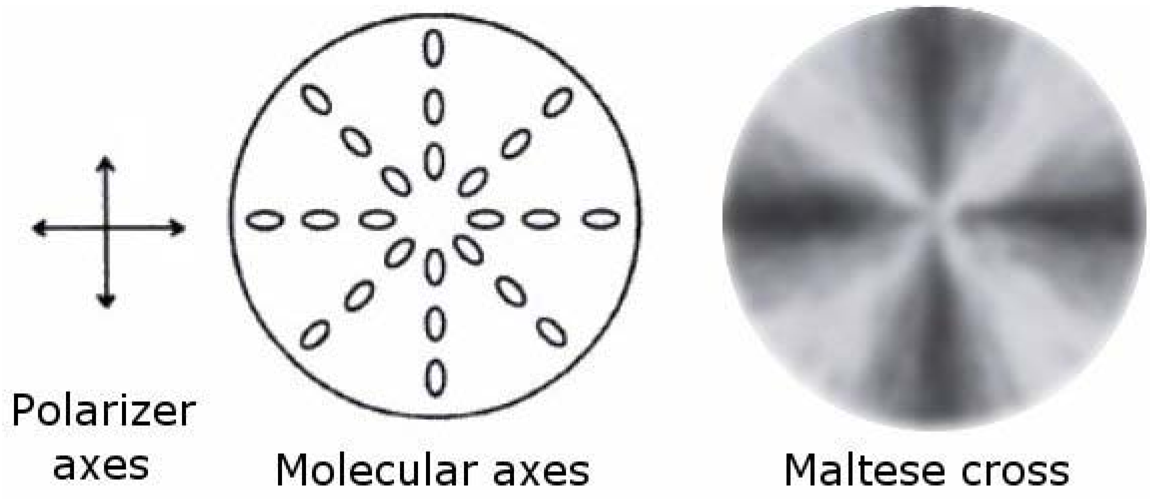
Changes in mechanical properties of polymers upon formation of spherulites however strongly depend on the size and density of the spherulites. A representative example is shown in the figure demonstrating that the strain at failure rapidly decreases with the increase in the spherulite size and thus with the decrease in their number in isotactic polypropylene. Similar trends are observed for tensile strength, yield stress and toughness. Increase in the total volume of the spherulites results in their interaction as well as shrinkage of the polymer, which becomes brittle and easily cracks under load along the boundaries between the spherulites.

Optical



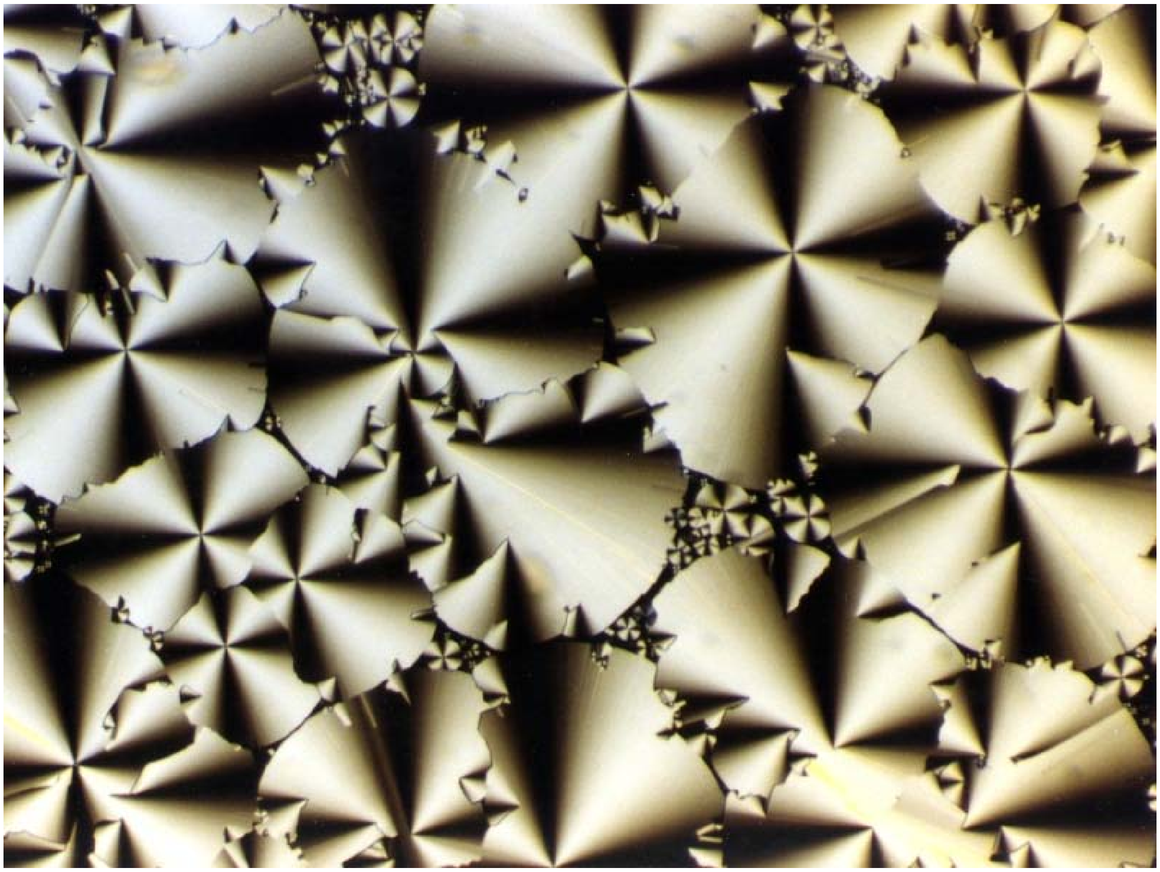
A spherulite embedded into a mosaic mesogen viewed between crossed polarizers.

Alignment of the polymer molecules within the lamellae results in birefringence producing a variety of colored patterns when spherulites are viewed between crossed polarizers in an optical microscope. In particular, the so-called "Maltese cross" is often present which consists of four dark perpendicular cones diverging from the origin, sometimes with a bright center (front picture). Its formation can be explained as follows. Linear polymer chains can be regarded as a linear polarizers. If their direction coincides with that of one of the crossed polarizers then little light is transmitted; the transmission is increased when the chains make a non-zero angle with both polarizers, and the induced transmittance is dependent on the wavelength, partly because of the absorption properties of the polymer.



A schematic of Maltese cross formation

This effect results in the dark perpendicular cones (Maltese cross) and colored brighter regions in between them in the front and right pictures. It reveals that the molecular axis of the polymer molecules in the spherules is either normal or perpendicular to the radius vector, i.e. molecular orientation is uniform when going along a line from the spherulite center to its edge along its radius. However, this orientation changes with rotation angle. The pattern may be different (bright or dark) for the center of the spherulites indicating misorientation of the molecules in the nucleation seeds of individual spherulites.



Spherulites embedded into a mosaic mesogen viewed between crossed polarizers.

When spherulites were rotated in their plane, the corresponding Maltese cross patterns did not change, indicating that the molecular arrangement is homogeneous versus the polar angle. From the birefringence point of view, spherulites can be positive or negative. This distinction depends not on the orientation of the molecules (parallel or perpendicular to the radial direction) but to the orientation of the major refractive index of the molecule relative to the radial vector. The spherulite polarity depends on the constituent molecules, but it can also change with temperature.

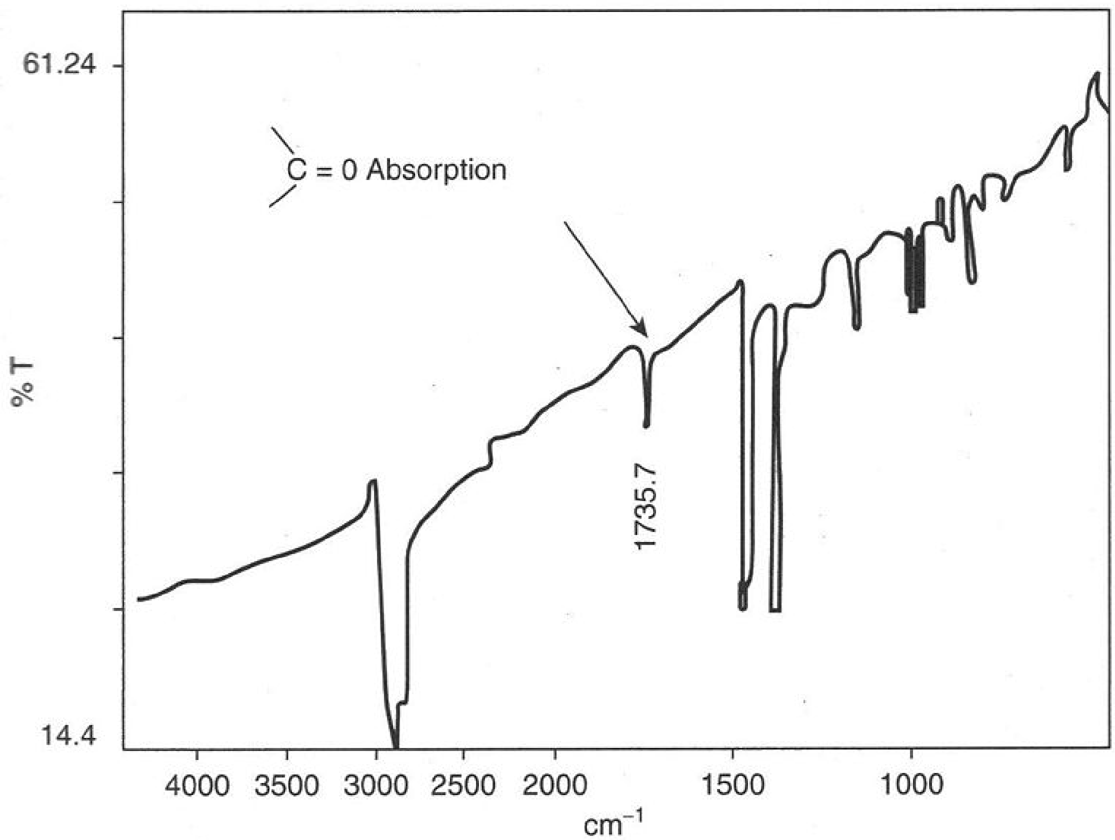
Chapter 4

Forensic Polymer Engineering

The study of failure in polymeric products is called **forensic polymer engineering**. The topic includes the fracture of plastic products, or any other reason why such a product fails in service, or fails to meet its specification. The subject focuses on the material evidence from crime or accident scenes, seeking defects in those materials that might explain why an accident occurred, or the source of a specific material to identify a criminal. Many analytical methods used for polymer identification may be used in investigations, the exact set being determined by the nature of the polymer in question, be it thermoset, thermoplastic, elastomeric or composite in nature.

One aspect is the analysis of trace evidence such as skid marks on exposed surfaces, where contact between dissimilar materials leaves material traces of one left on the other. Provided the traces can be analyzed successfully, then an accident or crime can often be reconstructed.

Methods of analysis



IR spectrum showing carbonyl absorption due to oxidative degradation of polypropylene

Thermoplastics can be analysed using infra-red spectroscopy, ultraviolet–visible spectroscopy, nuclear magnetic resonance spectroscopy and the environmental scanning electron microscope. Failed samples can either be dissolved in a suitable solvent and examined directly (UV, IR and NMR spectroscopy) or be a thin film cast from solvent or cut using microtomy from the solid product. Infra-red spectrosocpy is especially useful for assessing oxidation of polymers, such as the polymer degradation caused by faulty injection moulding. The spectrum shows the characteristic carbonyl group produced by oxidation of polypropylene, which made the product brittle. It was a critical part of a crutch, and when it failed, the user fell and injured herself very seriously. The spectrum was obtained from a thin film cast from a solution of a sample of the plastic taken from the failed forearm crutch.

Microtomy is preferable since there are no complications from solvent absorption, and the integrity of the sample is partly preserved. Thermosets, composites and elastomers can often be examined using only microtomy owing to the insoluble nature of these materials.

Fracture

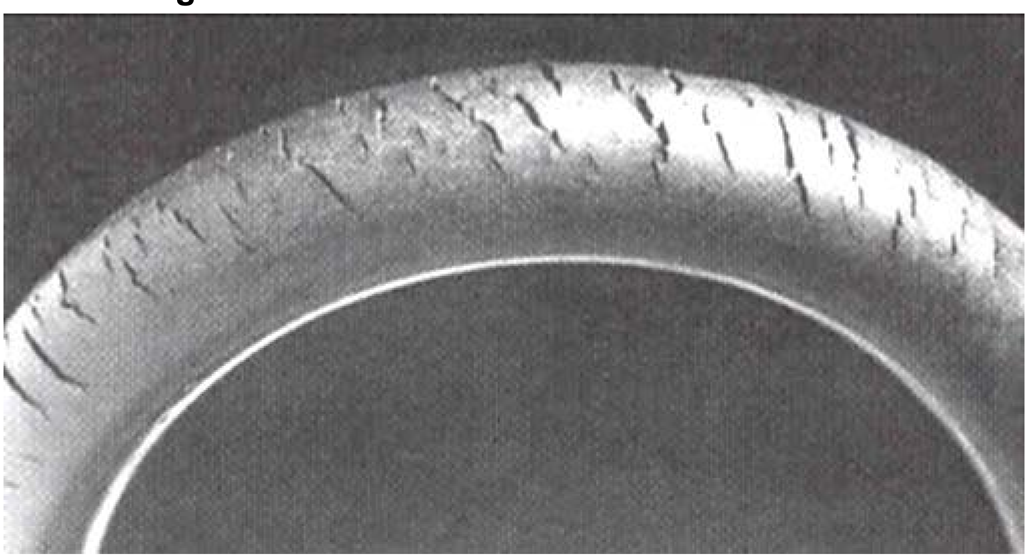
Fractured products can be examined using fractography, an especially useful method for all broken components using macrophotography and optical microscopy. Although polymers usually possess quite different properties to metals, ceramics and glasses, they are just as susceptible to failure from mechanical overload, fatigue and stress corrosion cracking if products are poorly designed or manufactured.

Scanning electron microscopy or ESEM is especially useful for examining fracture surfaces and can also provide elemental analysis of viewed parts of the sample being investigated. It is effectively a technique of microanalysis and valuable for examination of trace evidence. On the other hand, colour rendition is absent in ESEM, and there is no information provided about the way in which those elements are bonded to one another. Specimens will be exposed to a partial vacuum, so any volatiles may be removed, and surfaces may be contaminated by substances used to attach the sample to the mount.

Examples

Many polymers are attacked by specific chemicals in the environment, and serious problems can arise, including road accidents and personal injury. Polymer degradation leads to sample embrittlement, and fracture under low applied loads.

Ozone cracking

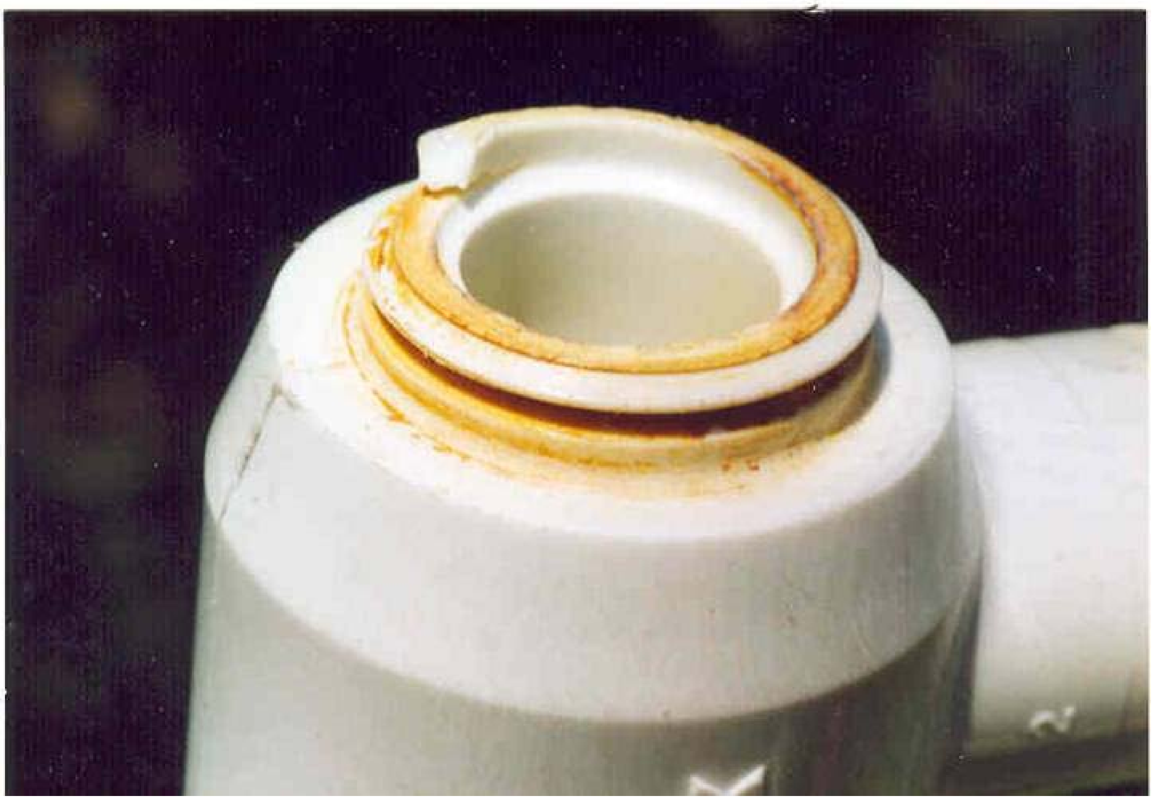


Ozone cracking in Natural rubber tubing

Polymers for example, can be attacked by aggressive chemicals, and if under load, then cracks will grow by the mechanism of stress corrosion cracking. Perhaps the oldest known example is the ozone cracking of rubbers, where traces of ozone in the atmosphere attack double bonds in the chains of the materials. Elastomers with double bonds in their chains include natural rubber, nitrile rubber and styrene-butadiene rubber.

They are all highly susceptible to ozone attack, and can cause problems like vehicle fires (from rubber fuel lines) and tyre blow-outs. Nowadays, anti-ozonants are widely added to these polymers, so the incidence of cracking has dropped. However, not all safety-critical rubber products are protected, and, since only ppb of ozone will start attack, failures are still occurring.

Chlorine-induced cracking

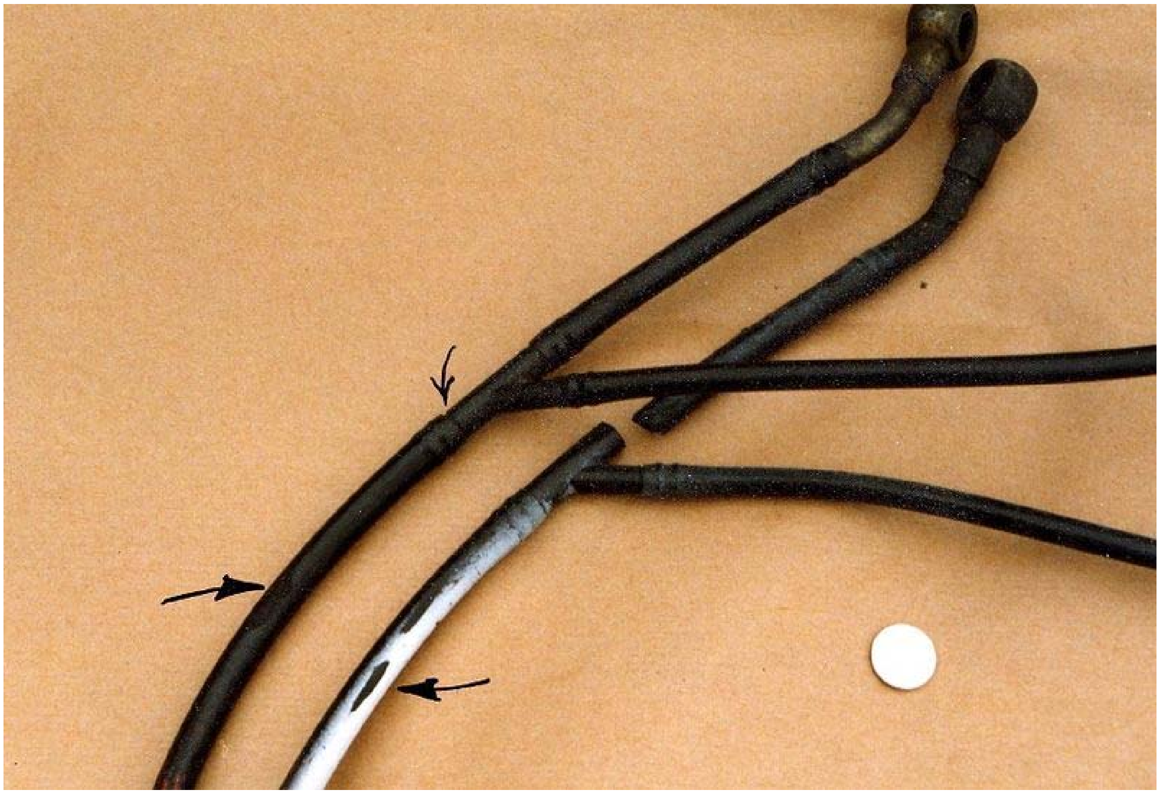


chlorine attack of acetal resin plumbing joint

Another highly reactive gas is chlorine, which will attack susceptible polymers such as acetal resin and polybutylene pipework. There have been many examples of such pipes and acetal fittings failing in properties in the USA as a result of chlorine-induced cracking. Essentially the gas attacks sensitive parts of the chain molecules (especially secondary , tertiary or allylic carbon atoms), oxidising the chains and ultimately causing chain cleavage. The root cause is traces of chlorine in the water supply, added for its anti-bacterial action, attack occurring even at parts per million traces of the dissolved gas. The chlorine attacks weak parts of a product, and, in the case of an acetal resin junction in a water supply system, it is the thread roots that were attacked first, causing a brittle crack to grow. The discoloration on the fracture surface was caused by deposition of carbonates from the hard water supply, so the joint had been in a critical state for many months.

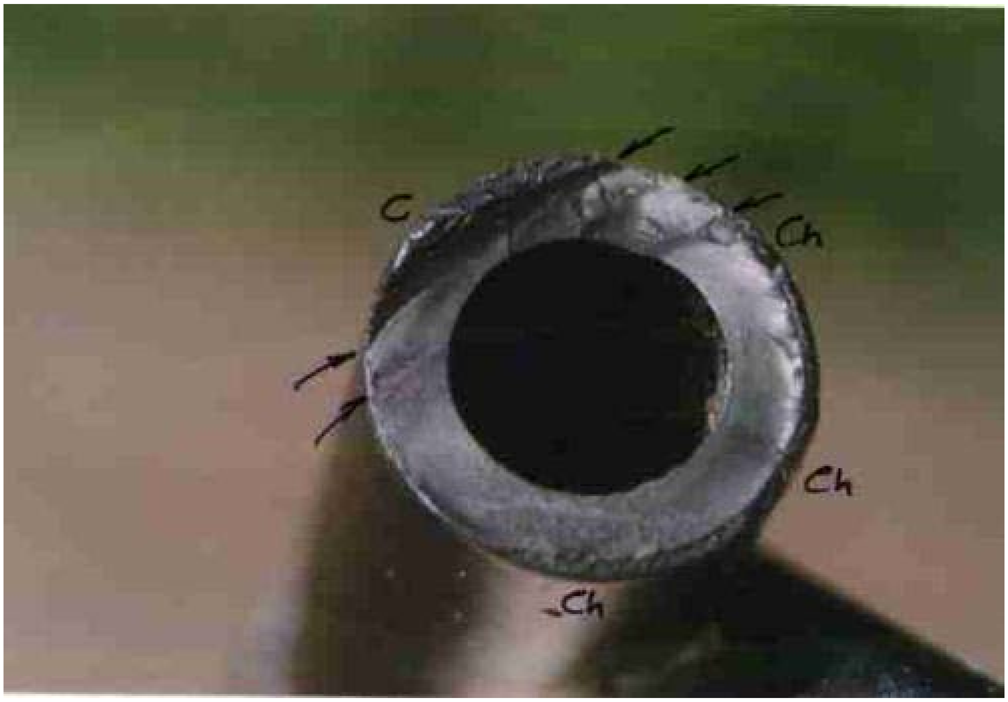
Hydrolysis

Most step-growth polymers can suffer hydrolysis in the presence of water, often a reaction catalysed by acid or alkali. Nylon for example, will degrade and crack rapidly if exposed to strong acids, a phenomenon well known to ladies who accidentally spill acid onto their tights.



Failed fuel pipe at right from road traffic accident

The broken fuel pipe caused a serious accident when diesel fuel poured out from a van onto the road. A following car skidded and the driver was seriously injured when she collided with an oncoming lorry. Scanning electron microscopy or SEM showed that the nylon connector had fractured by stress corrosion cracking due to a small leak of battery acid. Nylon is susceptible to hydrolysis in contact with sulfuric acid, and only a small leak of acid would have sufficed to start a brittle crack in the injection moulded connector by a mechanism known as stress corrosion cracking, or SCC.

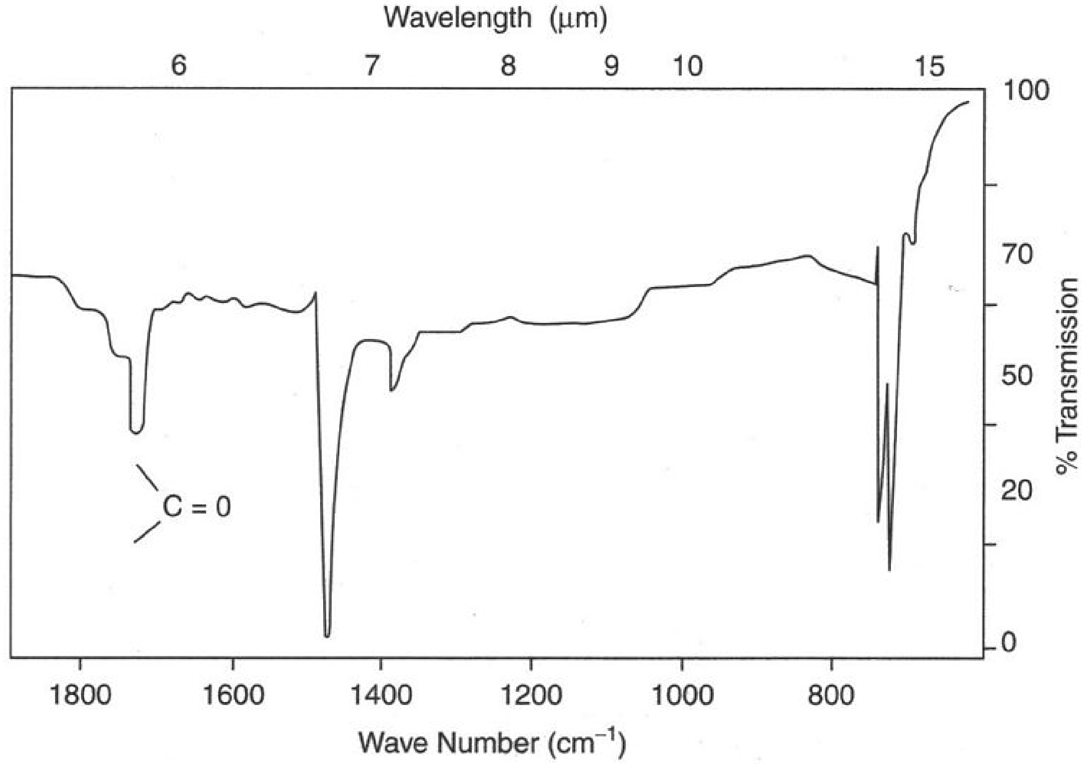


Close-up of broken fuel pipe

The crack took about 7 days to grow across the diameter of the tube, hence the van driver should have seen the leak well before the crack grew to a critical size. He did not, therefore resulting in the accident. The fracture surface showed a mainly brittle surface with striations indicating progressive growth of the crack across the diameter of the pipe. Once the crack had penetrated the inner bore, fuel started leaking onto the road. Diesel is especially hazardous on road surfaces because it forms a thin oily film that cannot be seen easily by drivers. It is akin to black ice in lubricity, so skids are common when diesel leaks occur. The insurers of the van driver admitted liability and the injured driver was compensated.

Polycarbonate is susceptible to alkali hydrolysis, the reaction simply depolymerising the material. Polyesters are prone to degrade when treated with strong acids, and in all these cases, care must be taken to dry the raw materials for processing at high temperatures to prevent the problem occurring.

UV degradation



IR spectrum showing carbonyl absorption due to UV degradation of polyethylene

Many polymers are also attacked by UV radiation at vulnerable points in their chain structures. Thus polypropylene suffers severe cracking in sunlight unless anti-oxidants are added. The point of attack occurs at the tertiary carbon atom present in every repeat unit, causing oxidation and finally chain breakage. Polyethylene is also susceptible to UV degradation, especially those variants that are branched polymers such as LDPE. The branch points are tertiary carbon atoms, so polymer degradation starts there and results in chain cleavage, and embrittlement. In the example shown at left, carbonyl groups were easily detected by IR spectroscopy from a cast thin film. The product was a road cone that had cracked in service, and many similar cones also failed because an anti-UV additive had not been used.

Chapter 5

Electroactive Polymers

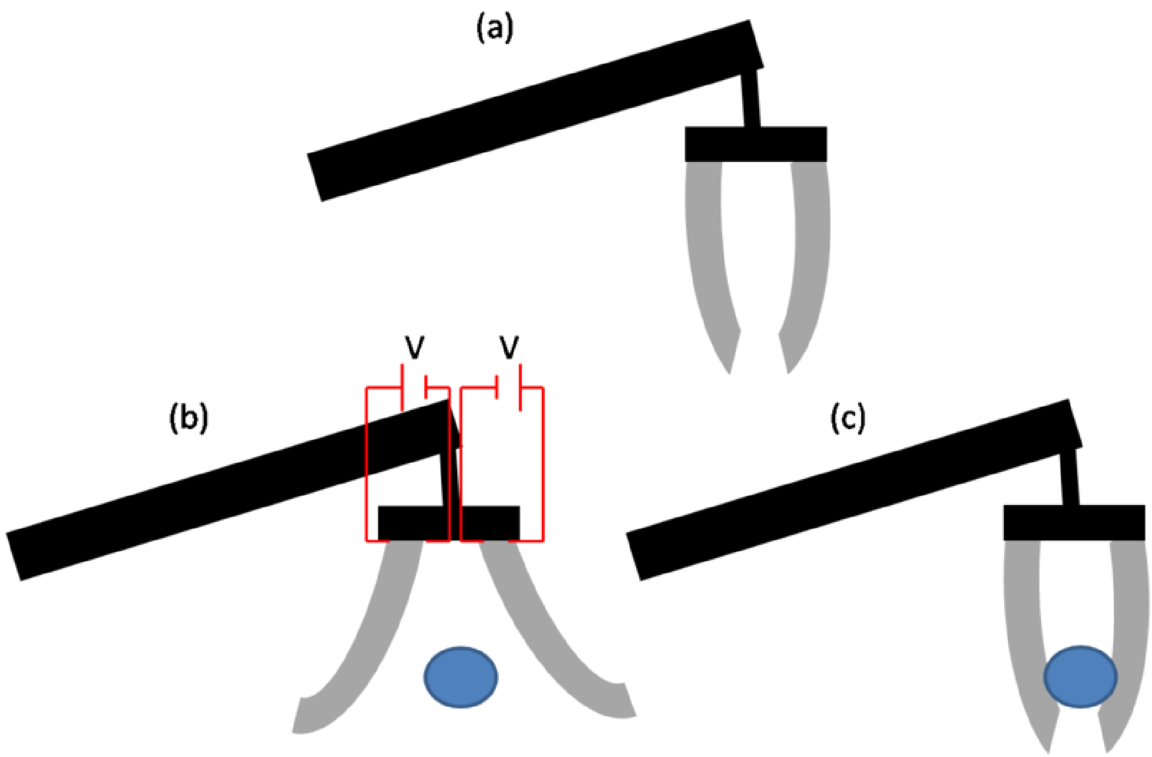


Figure 1: Cartoon drawing of an EAP gripping device. (a) A voltage is applied and the EAP fingers deform in order to surround the ball. (b) When the voltage is removed the EAP fingers return to their original shape and grip the ball. (c)

Electroactive Polymers, or EAPs, are polymers that exhibits a change in size or shape when stimulated by an electric field. The most common applications of this type of material are in actuators and sensors. A typical characteristic property of an EAP is that they will undergo a large amount of deformation while sustaining large forces. The majority of historic actuators are made of ceramic piezoelectric materials. While these materials are able to withstand large forces, they commonly will only deform a fraction of a percent. In the late 1990s, it has been demonstrated that some EAPs can exhibit up to a 380% strain, which is much more than any ceramic actuator. Another one of the most common applications for EAPs is in the field of robotics in the development of artificial muscles. Due to this being one of the most common and attractive applications, EAPs are often referred to as artificial muscles. A cartoon drawing of a gripping device using EAPs as "fingers" to grip a ball is depicted in Figure 1.

History of EAPs

The field of EAPs emerged back in 1880, when Wilhelm Roentgen designed an experiment in which he tested the effect of an electrical current on the mechanical properties of a rubber band. The rubber band was fixed at one end and was attached to a mass at the other. It was then charged and discharged to study the change in length with electrical current. Sacerdote followed up on Roentgen's experiment by formulating a theory on strain response to an applied electric field in 1899. It wasn't until the year 1925 that the first piezoelectric polymer was discovered (Electret). Electret was formed by combining carnauba wax, rosin and beeswax, and then cooling the solution while it is subject to an applied DC electrical bias. The mixture would then solidify into a polymeric material that exhibited a piezoelectric effect.

Polymers that respond to environmental conditions other than an applied electrical current have also been a large part of this area of study. In 1949, Katchalsky et. al. demonstrated that when collagen filaments are dipped in acid or alkali solutions they would respond with a change in volume. The collagen filaments were found to expand in an acidic solution and contract in an alkali solution. Although other stimuli (such as pH) have been investigated, due to its ease and practicality most research has been devoted to developing polymers that respond to electrical stimuli in order to mimic biological systems.

It wasn't until the late 1960s when the next major breakthrough in EAPs was observed. In 1969, Kawai was able to demonstrate that polyvinylidene fluoride (PVDF) exhibits a large piezoelectric effect. This sparked research interest in developing other polymers systems that would show a similar effect. In 1977, the first electrically conducting polymers were discovered by Hideki Shirakawa et.al. Shirakawa along with Alan MacDiarmid and Alan Heeger demonstrated that polyacetylene was electrically conductive, and that by doping it with iodine vapor, they could enhance its conductivity by 8 orders of magnitude. Thus the conductance was close to that of a metal. By the late 1980s a number of other polymers had been shown to exhibit a piezoelectric effect or were demonstrated to be conductive.

In the early 1990s, ionic polymer-metal composites were developed and shown to exhibit electroactive properties far superior to previous EAPs. The major advantage of IPMCs was that they were able to show activation (deformation) at voltages as low as 1 or 2 volts. This is orders of magnitude less than any previous EAP. Not only was the activation energy for these materials much lower, but they could also undergo much larger deformations. IMPCs were shown to exhibit anywhere up to 380% strain, orders of magnitude larger than previously developed EAPs. In 1999, one of the pioneers of the field of robotics and artificial muscles, Yoseph Bar-Cohen, proposed the Armwrestling Match of EAP Robotic Arm Against Human Challenge. This was a challenge in which research groups around the world competed to design a robotic arm consisting of EAP muscles that could defeat a human in an arm wrestling match. The first challenge was held at the Electroactive Polymer Actuators and Devices Conference in 2005. Another major milestone of the field is that the first commercially developed device including EAPs as an artificial muscle was produced in 2002 by Eamex in Japan. This device was a fish that is able to swim on its own, moving its tail using an EAP muscle. But the progress in practical development is not satisfactory, probably due to misleading in fundamental research.

Types of Electroactive Polymers

EAP can have several configurations, but are generally divided in two principal classes: Dielectric and Ionic.

Dielectric EAPs

- Dielectric EAPs, are materials in which actuation is caused by electrostatic forces between two electrodes which squeeze the polymer. Dielectric elastomers are capable of very high strains and are fundamentally a capacitor that changes its capacitance when a voltage is applied by allowing the polymer to compress in thickness and expand in area due to the electric field. This type of EAP typically requires a large actuation voltage to produce high electric fields (hundreds to thousands of volts), but very low electrical power consumption. Dielectric EAPs require no power to keep the actuator at a given position. Examples are electrostrictive polymers and dielectric elastomers.

Ferroelectric Polymers

Ferroelectric Polymers are a group of crystalline polar polymers that are also ferroelectric, meaning that they maintain a permanent electric polarization that can be reversed, or switched, in an external electric field. Ferroelectric polymers, such as polyvinylidene fluoride(PVDF), are used in acoustic transducers and electromechanical actuators because of their inherent piezoelectric response, and as heat sensors because of their inherent pyroelectric response.

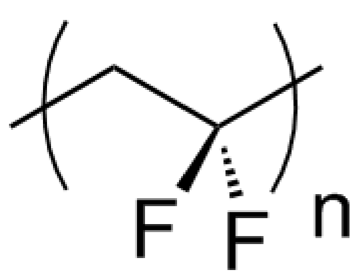


Figure 1: Structure of Poly(vinylidene fluoride)

Electrostrictive Graft Polymers

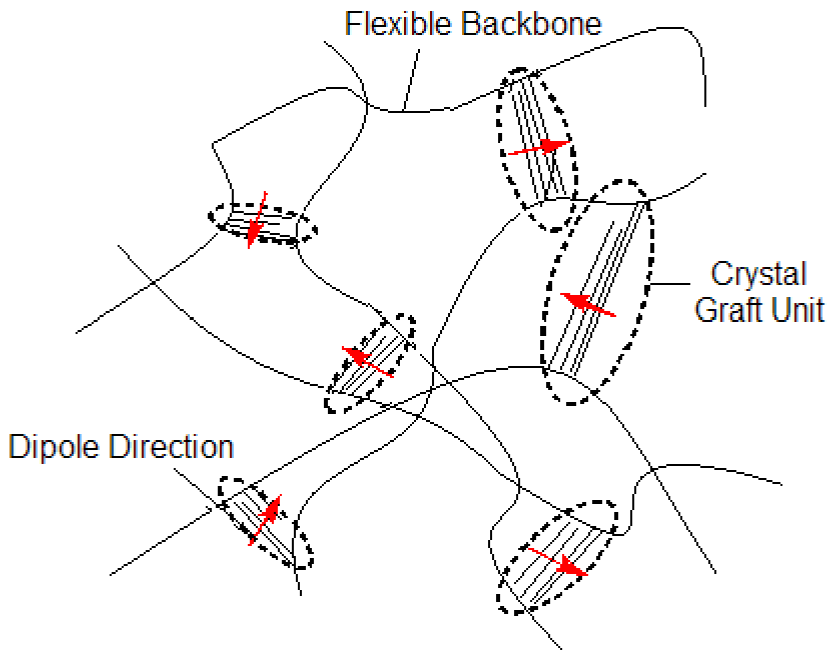


Figure 2: Cartoon of an electrostrictive graft polymer.

Electrostricive graft polymers consist of flexible backbone chains with branching side chains. The side chains on neighboring backbone polymers cross link and form crystal units. The backbone and side chain crystal units can then form polarized monomers, which contain atoms with partial charges and generate dipole moments, shown in Figure 2. When an electrical field is applied, a force is applied to each partial charge and causes rotation of the whole polymer unit. This rotation causes electrostrictive strain and deformation of the polymer.

Liquid Crystalline Polymers

Main-chain liquid crystalline polymers have mesogenic groups linked to each other by a flexible spacer. The mesogens within a backbone form the mesophase structure causing the polymer itself to adopt a conformation compatible with the structure of the mesophase. The direct coupling of the liquid crystalline order with the polymer conformation has given main-chain liquid crystalline elastomers a large amount of interest. The synthesis of highly oriented elastomers leads to have a large strain thermal actuation along the polymer chain direction with temperature variation resulting in unique mechanical properties and potential applications as mechanical actuators.

Ionic EAPs

- Ionic EAPs, in which actuation is caused by the displacement of ions inside the polymer. Only a few volts are needed for actuation, but the ionic flow implies a higher electrical power needed for actuation, and energy is needed to keep the actuator at a given position. Examples of ionic EAPS are conductive polymers, ionic polymer-metal composites (IPMCs), and responsive gels. Yet another example is a Bucky gel actuator, which is a polymer-supported layer of polyelectrolyte material consisting of an ionic liquid sandwiched between two electrode layers consisting of a gel of ionic liquid containing single-wall carbon nanotubes. As the name implies, these gel actuators can also be made with bucky balls instead of nanotubes.

Electrorheological Fluid

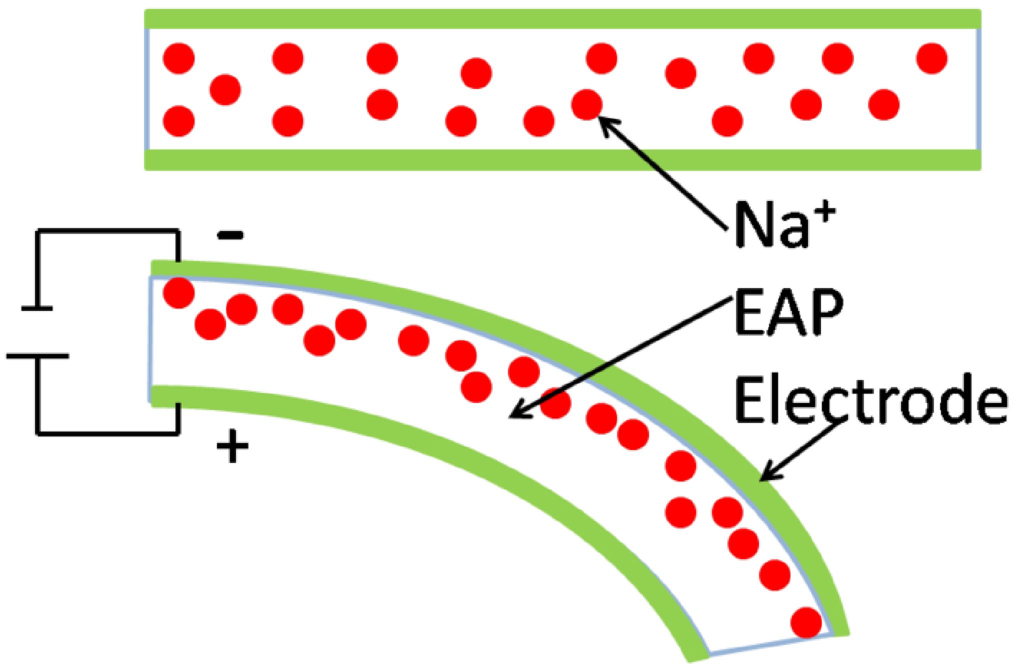


Figure 3: The cations in the ionic polymer-metal composite are randomly oriented in the absence of an electric field. Once a field is applied the cations gather to the side of the polymer in contact with the anode causing the polymer to bend.

Electrorheological fluids change the viscosity of a solution with the application of an electric field. The fluid is a suspension of polymers in a low dielectric-constant liquid. With the application of a large electric field the viscosity of the suspension increases. Potential applications of these fluids include shock absorbers, engine mounts and acoustic dampers.

Ionic polymer-metal composite

Ionic polymer-metal composites consist of a thin ionomeric membrane with noble metal electrodes plated on its surface. It also has cations to balance the charge of the anions fixed to the polymer backbone. They are very active actuators that show very high deformation at low applied voltage and show low impedance. Ionic polymer-metal composites work through electrostatic attraction between the cationic counter ions and the anode of the applied electric field, a schematic representation is shown in Figure 3.

These types of polymers show the greatest promise for bio-mimetic uses as collagen fibers are essentially composed of natural charged ionic polymers. Nafion and Flemion are commonly used ionic polymer metal composites.

Comparison of Electronic and Ionic EAPs

Dielectronic polymers are able to hold their induced displacement while activated under a DC voltage. This allows dielectronic polymers to be considered for robotic applications. These types of materials also have high mechanical energy density and can be operated in air without a major decrease in performance. However, dielectronic polymers require very high activation fields (>10 v/um) that are close to the breakdown level.

The activation of ionic polymers, on the other hand, requires only 1-2 volts. They however need to maintain wetness, though some polymers have been developed as self contained encapsulated activators which allows their use in dry environments. Ionic polymers also have a low electromechanical coupling. They are however ideal for the bio-mimetic devices.

Characterization

While there are many different ways electroactive polymers can be characterized, only three will be addressed here: stress-strain curve, dynamic mechanical thermal analysis, and dielectric thermal analysis.

Stress-Strain Curve

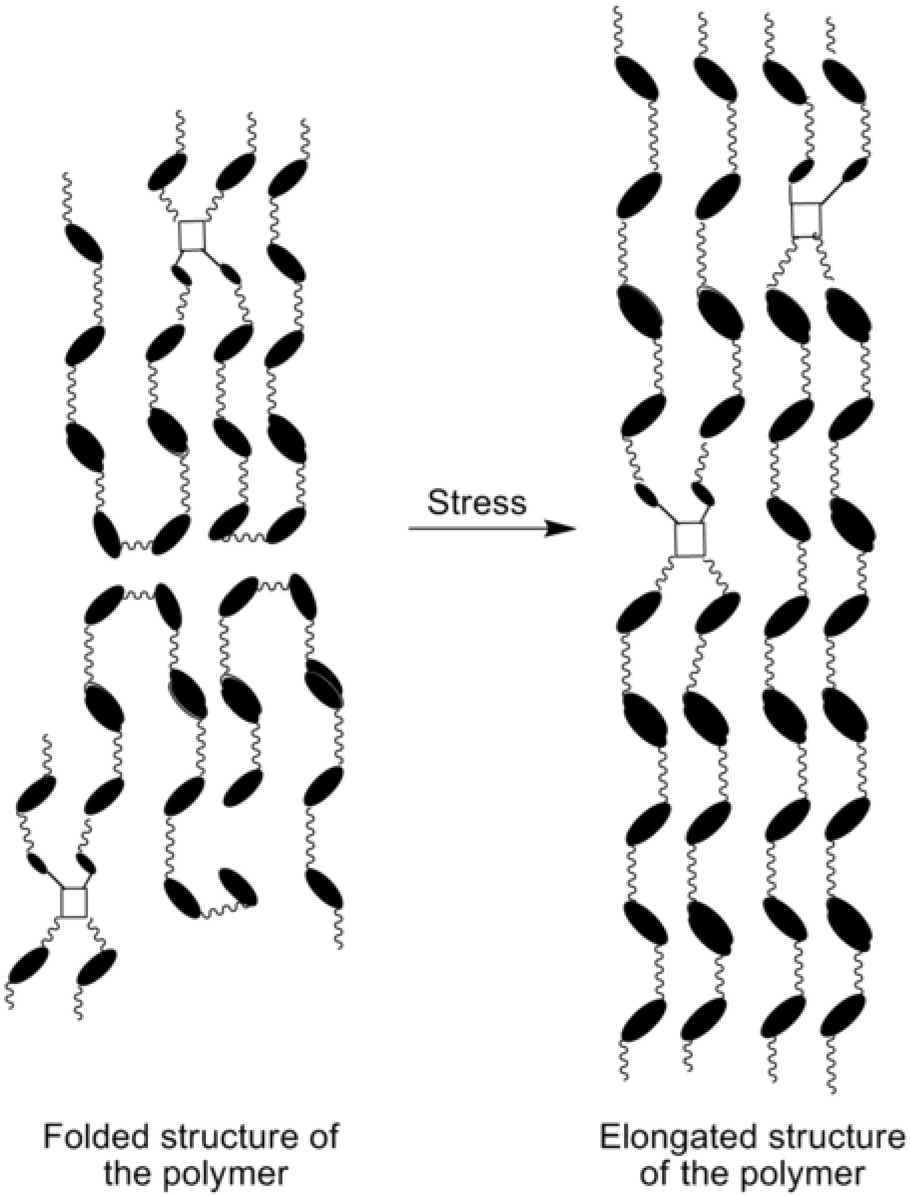


Figure 4: The unstressed polymer spontaneously forms a folded structure, upon application of a stress the polymer regains its original length.

Stress strain curves provide information about the polymer's mechanical properties such as the brittleness, elasticity and yield strength of the polymer. This is done by providing a force to the polymer at a uniform rate and measuring the deformation that results. An example of this deformation is shown in Figure 4. This technique is useful for determining the type of material (brittle, tough, etc.), but it is a destructive technique as the stress is increased until the polymer fractures.

Dynamic mechanical thermal analysis (DMTA)

Both dynamic mechanical analysis is a non destructive technique that is useful in understanding the mechanism of deformation at a molecular level. In DMTA a sinusoidal stress is applied to the polymer, and based on the polymer's deformation the elastic modulus and damping characteristics are obtained (assuming the polymer is a damped harmonic oscillator). Elastic materials take the mechanical energy of the stress and convert it into potential energy which can later be recovered. An ideal spring will use all the potential energy to regain its original shape (no dampening), while a liquid will use all the potential energy to flow, never returning to its original position or shape (high dampening). A viscoeleastic polymer will exhibit a combination of both types of behavior.

Dielectric thermal analysis (DETA)

DETA is similar to DMTA, but instead of an alternating mechanical force an alternating electric field is applied. The applied field can lead to polarization of the sample, and if the polymer contains groups that have permanent dipoles (as in Figure 2), they will align with the electrical field. The permittivity can be measured from the change in amplitude and resolved into dielectric storage and loss components. The electric displacement field can also be measured by following the current. Once the field is removed, the dipoles will relax back into a random orientation.

Applications of EAP

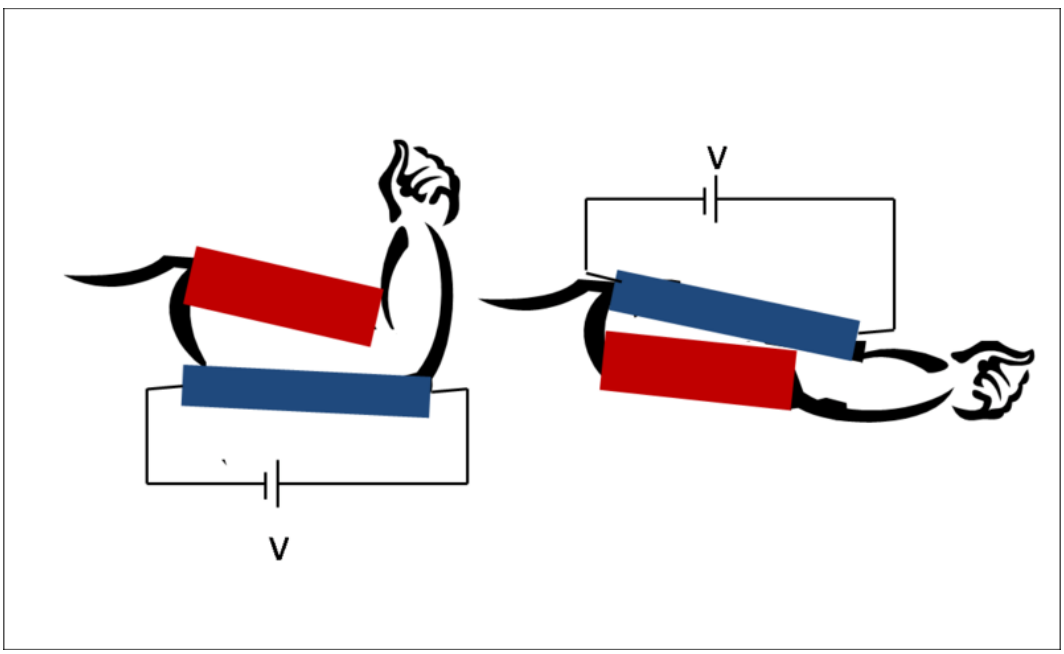


Figure 5: Cartoon drawing of an arm controlled by EAPs. When a voltage is applied (blue muscles) the polymer expands. When the voltage is removed (red muscles) the polymer returns to its original state.

EAP materials can be easily manufactured into various shapes due to the ease in processing many polymeric materials, making them very versatile materials. One potential application for EAPs is that they can potentially be integrated into microelectromechanical systems (MEMS) to produce smart actuators. As the most prospective practical research direction, EAPs have been utilized in artificial muscles. Their ability to emulate the operation of biological muscles with high fracture toughness, large actuation strain and inherent vibration damping draw the attention of scientists in this field.

In recent years, "electro active polymers for refreshable Braille displays" has emerged to aid the visually impaired in fast reading and computer assisted communication. This concept is based on using an EAP actuator configured in an array form. Rows of electrodes on one side of an EAP film and columns on the other activate individual elements in the array. Each element is mounted with a Braille dot and is lowered by applying a voltage across the thickness of the selected element, causing local thickness reduction. Under computer control, dots would be activated to create tactile patterns of highs and lows representing the information to be read.

Small pumps can also be achieved by applying EAP materials. These pumps could be used for drug delivery, microfluidic devices, active flow control, and a multitude of consumer applications. The most likely configuration for a pump based on actuators would be a dual diaphragm device. The advantages that an ionomeric pump could offer would be low voltage (battery) operation, extremely low noise signature, high system efficiency, and highly accurate control of flow rate.

Another technology that can benefit from the unique properties of EAP actuators is optical membranes. Due to their low modulus, the mechanical impedance of the actuators, they are well-matched to common optical membrane materials. Also, a single EAP actuator is capable of generating displacements that range from microns to centimeters. For this reason, these materials can be used for static shape correction and jitter suppression. These actuators could also be used to correct for optical aberrations due to atmospheric interference.

Since these materials exhibit excellent electroactive character, EAP materials show potential in biomimetic-robot research, stress sensors and acoustics field, which will make EAPs become a more attractive study topic in the near future. They have been used for various actuators such as face muscles and arm muscles in humanoid robots.

Future Directions

The field of EAPs is far from mature, which leaves several issues that still need to be worked on. The performance and long-term stability of the EAP should be improved by designing a water impermeable surface. This will prevent the evaporation of water contained in the EAP, and also reduce the potential loss of the positive counter ions when the EAP is operating submerged in an aqueous environment. Improved surface conductivity should be explored using methods to produce a defect-free conductive surface. This could possibly be done using metal vapor deposition or other doping methods. It may also be possible to utilize conductive polymers to form a thick conductive layer. Heat resistant EAP would be desirable to allow operation at higher voltages without damaging the internal structure of the EAP due to the generation of heat in the EAP composite. Development of EAPs in different configurations (e.g., fibers and fiber bundles), would also be beneficial, in order to increase the range of possible modes of motion.

Chapter 6

Fire-Safe Polymers

Fire-safe polymers are polymers that are resistant to degradation at high temperatures. There is need for fire-resistant polymers in the construction of small, enclosed spaces such as skyscrapers, boats, and airplane cabins. In these tight spaces, ability to escape in the event of a fire is compromised, increasing fire risk. In fact, some studies report that about 20% of victims of airplane crashes are killed not by the crash itself but by ensuing fires. Fire-safe polymers also find application as adhesives in aerospace materials, insulation for electronics, and in military materials such as canvas tenting.

Some fire-safe polymers naturally exhibit an intrinsic resistance to decomposition, while others are synthesized by incorporating fire-resistant additives and fillers. Current research in developing fire-safe polymers is focused on modifying various properties of the polymers such as ease of ignition, rate of heat release, and the evolution of smoke and toxic gases. Standard methods for testing polymer flammability vary among countries; in the United States common fire tests include the UL 94 small-flame test, the ASTM E 84 Steiner Tunnel, and the ASTM E 622 National Institute of Standards and Technology (NIST) smoke chamber. Research on developing fire-safe polymers with more desirable properties is concentrated at the University of Massachusetts Amherst and at the Federal Aviation Administration where a long-term research program on developing fire-safe polymers was begun in 1995. The Center for UMass/Industry Research on Polymers (CUMIRP) was established in 1980 in Amherst, MA as a concentrated cluster of scientists from both academia and industry for the purpose of polymer science and engineering research.

History

Early History

Controlling the flammability of different materials has been a subject of interest since 450 B.C. when Egyptians attempted to reduce the flammability of wood by soaking it in potassium aluminum sulfate (alum). Between 450 B.C. and the early 20th century, other materials used to reduce the flammability of different materials included mixtures of alum and vinegar; clay and hair; clay and gypsum; alum, ferrous sulfate, and gypsum;

and ammonium chloride, ammonium phosphate, borax, and various acids. These early attempts found application in reducing the flammability of wood for military materials, theater curtains, and other textiles, for example. Important milestones during this early work include the first patent for a mixture for controlling flammability issued to Obadiah Wyld in 1735, and the first scientific exploration of controlling flammability, which was undertaken by Joseph Louis Gay-Lussac in 1821.

Developments Since WWII

Research on fire-retardant polymers was bolstered by the need for new types of synthetic polymers in World War II. The combination of a halogenated paraffin and antimony oxide was found to be successful as a fire retardant for canvas tenting. Syntheses of polymers, such as polyesters, with fire retardant monomers were also developed around this time. Incorporating flame-resistant additives into polymers became a common and relatively cheap way to reduce the flammability of polymers, while synthesizing intrinsically fire-resistant polymers has remained a more expensive alternative, although the properties of these polymers are usually more efficient at deterring combustion.

Polymer Combustion

General Mechanistic Scheme

Traditional polymers decompose under heat and produce combustible products; thus, they are able to originate and easily propagate fire (as shown in Figure 1).

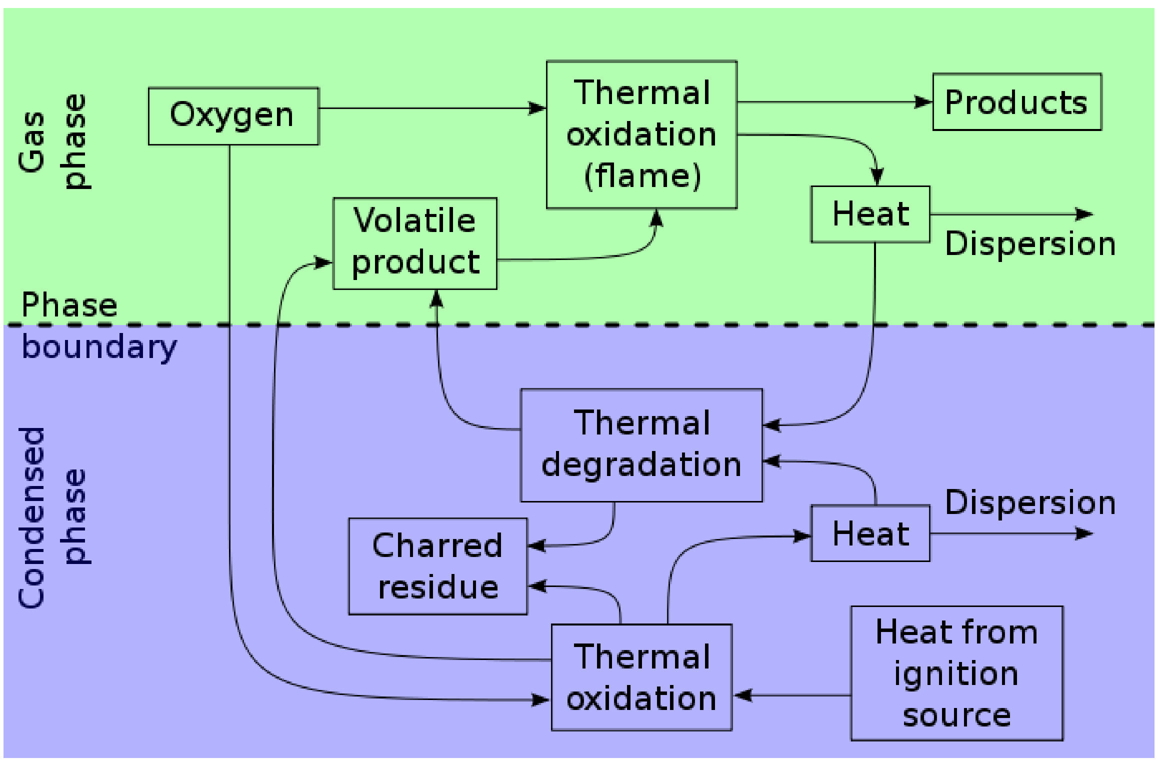


Figure 1: A general scheme of polymer combustion.

The combustion process begins when heating a polymer yields volatile products. If these products are sufficiently concentrated, within the flammability limits, and at a temperature above the ignition temperature, then combustion proceeds. As long as the heat supplied to the polymer remains sufficient to sustain its thermal decomposition at a rate exceeding that required to feed the flame, combustion will continue.

Purpose and Methods of Fire-Retardant Systems

The purpose is to control heat below the critical level. To achieve this, one can create an endothermic environment, produce non-combustible products, or add chemicals that would remove fire-propagating radicals (H and OH), to name a few. These specific chemicals can be added into the polymer molecules permanently or as additives and fillers.

Role of Oxygen

Oxygen catalyzes the pyrolysis of polymers at low concentration and initiates oxidation at high concentration. Transition concentrations are different for different polymers. (e.g., polypropylene, between 5% and 15%). Additionally, polymers exhibit a structural-dependent relationship with oxygen. Some structures are intrinsically more sensitive to decomposition upon reaction with oxygen. The amount of access that oxygen has to the surface of the polymer also plays a role in polymer combustion. Oxygen is better able to interact with the polymer before a flame has actually been ignited.

Role of Heating Rate

In most cases, results from a typical heating rate (e.g. 10℃/min for mechanical thermal degradation studies) do not differ significantly from those obtained at higher heating rates. The extent of reaction can, however, be influenced by the heating rate. For example, some reactions may not occur with a low heating rate due to evaporation of the products.

Role of Pressure

Volatile products are removed more efficiently under low pressure, which means the stability of the polymer might have been compromised. Decreased pressure also slows down decomposition of high boiling products.

Intrinsically Fire-Resistant Polymers

The polymers that are most efficient at resisting combustion are those that are synthesized as intrinsically fire-resistant. However, these types of polymers can be difficult as well as costly to synthesize. Modifying different properties of the polymers can increase their intrinsic fire-resistance; increasing rigidity or stiffness, the use of polar monomers, and/or hydrogen bonding between the polymer chains can all enhance fire-resistance.

Linear, Single-Stranded Polymers With Cyclic Aromatic Components

Most intrinsically fire-resistant polymers are made by incorporation of aromatic cycles or heterocycles, which lend rigidity and stability to the polymers. Polyimides, polybenzoxazoles (PBOs), polybenzimidazoles, and polybenzthiazoles (PBTs) are examples of polymers made with aromatic heterocycles (Figure 2).

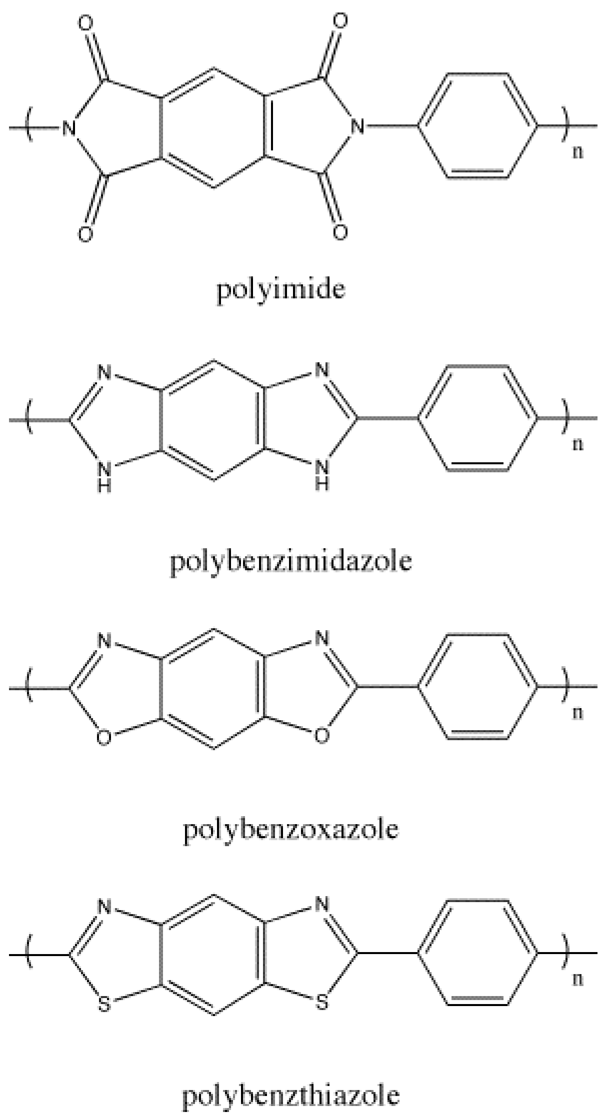


Figure 2: Different fire-resistant polymers made with aromatic heterocycles.

Polymers made with aromatic monomers have a tendency to condense into chars upon combustion, decreasing the amount of flammable gas that is released. Syntheses of these types of polymers generally employ prepolymers which are further reacted to form the fire-resistant polymers.

Ladder Polymers

Ladder polymers are a subclass of polymers made with aromatic cycles or heterocycles. Ladder polymers generally have one of two types of general structures, as shown in Figure 3.

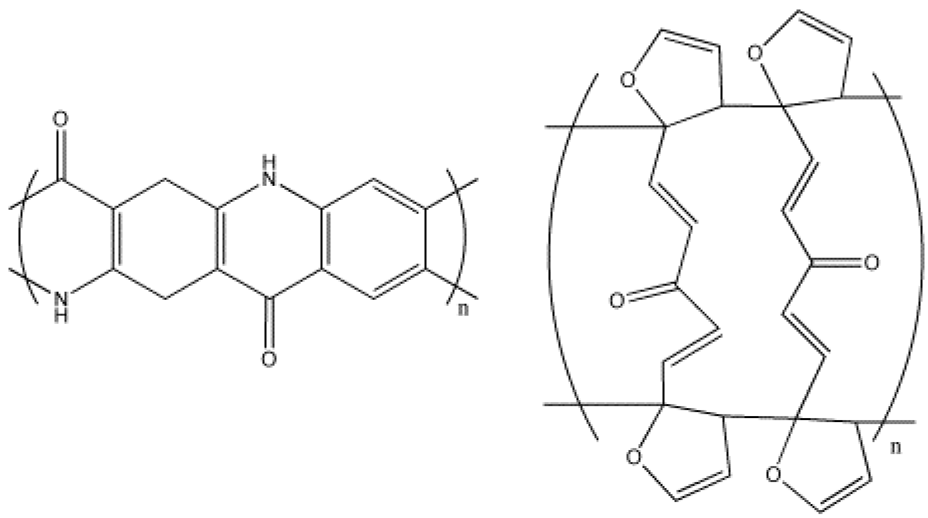


Figure 3: Two representative structures of different types of ladder polymers.

One type of ladder polymer links two polymer chains with periodic covalent bonds. In another type, the ladder polymer consists of a single chain that is double-stranded. Both types of ladder polymers exhibit good resistance to decomposition from heat because the chains do not necessarily fall apart if one covalent bond is broken. However, this makes the processing of ladder polymers difficult because they are not easily melted. These difficulties are compounded because ladder polymers are often highly insoluble.

Inorganic and Semiorganic Polymers

Inorganic and semiorganic polymers often employ silicon-nitrogen, boron-nitrogen, and phosphorus-nitrogen monomers. The non-burning characteristics of the inorganic components of these polymers contribute to their controlled flammability. For example, instead of forming toxic, flammable gasses in abundance, polymers prepared with incorporation of cyclotriphosphazene rings give a high char yield upon combustion. Polysialates (polymers containing frameworks of aluminum, oxygen, and silicon) are another type of inorganic polymer that can be thermally stable up to temperatures of 1300-1400°C.

Flame-Retardant Additives and Fillers

Additives are divided into two basic types depending on the interaction of the additive and polymer. Reactive flame retardants are compounds that are chemically built into the polymer. They usually contain heteroatoms. Additive flame retardants, on the other hand, are compounds that are not covalently bound to the polymer; the retardant and the polymer are just physically mixed together. At present, there are basically six elements being widely used in this field: boron, aluminum, phosphorus, antimony, chlorine, and bromine. One prominent advantage of these types of fire-safe polymers is that they are relatively easy to manufacture.

Natural Fiber-Containing Composites

Besides providing satisfactory mechanical properties and renewability, natural fibers are easier to obtain and much cheaper than man-made materials. Moreover, they are more environmentally friendly. Recent research focuses on application of different types of fire retardants during the manufacturing process as well as applications of fire retardants (especially intumescent coatings) at the finishing stage.

Nanocomposites

Nanocomposites have become a hotspot in the research of fire-safe polymers because of their relatively low cost and high flexibility for multifunctional properties. Gilman and colleagues did the pioneering work by demonstrating the improvement of fire-retardancy by having nanodispersed montmorillonite clay in the polymer matrix. Later, organomodified clays, TiO_2 nanoparticles, silica nanoparticles, layered double hydroxides, carbon nanotubes and polyhedral silsesquioxanes were proved to work as well. Recent research has suggested that combining nanoparticles with traditional fire retardants (e.g., intumescents) or with surface treatment (e.g., plasma treatment) effectively decreases flammability.

Problems with Additives and Fillers

Although effective at reducing flammability, flame-retardant additives and fillers have disadvantages as well. Their poor compatibility, high volatility and other deleterious effects can change properties of polymers. Besides, addition of many fire-retardants produces soot and carbon monoxide during combustion. Halogen-containing materials cause even more concerns on environmental pollution.

Chapter 7

Polymer Separators

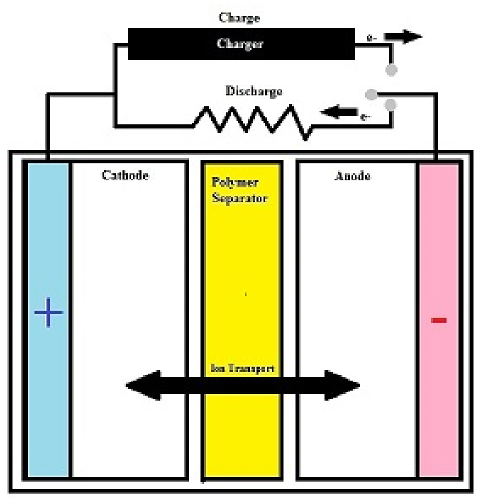


Diagram of a battery with a polymer separator.

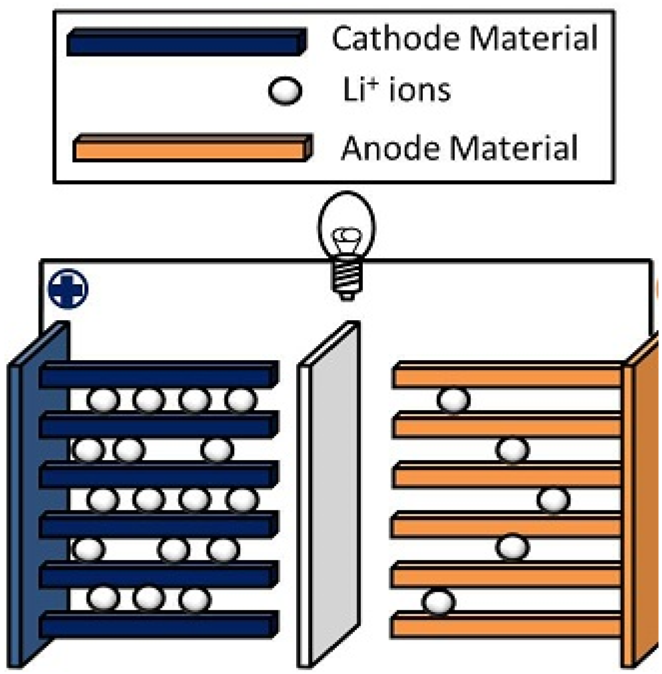
A **polymer separator** is a permeable membrane placed between the anode and cathode of a battery. The main function of a separator is to keep the positive and negative electrodes, the cathode and anode respectively, apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers which are needed to complete the circuit during the passage of current in an electrochemical cell.

Background

Polymer separators are critical components in liquid electrolyte batteries. The separator is placed between the positive and negative electrode in order to prevent physical contact of the electrodes while enabling ionic transport. A separator generally consists of a polymeric membrane forming a microporous layer. It must be chemically and electrochemically stable towards the electrolyte and electrode materials, while also being mechanically strong enough to withstand the high tension of battery construction. They are important to batteries because their structure and properties considerably affect the battery performance, including the batteries energy and power densities, cycle life, and safety.

History

Unlike many forms of technology, polymer separators were not developed specifically for batteries. They were instead a result of spin-offs of existing technologies, which is why most polymer separators are not optimized for many of the systems they are used in. Even though this may seem unfavorable, most polymer separators can be mass produced at a comparatively low cost, because they are based on existing forms of technologies. Dr. Yoshino et al. of the Asahi Kasei Corporation first developed a prototype of secondary lithium-ion batteries (LIBs) in 1983.



Schematic of a lithium ion battery.

These prototype rechargeable cells included two electrodes; the cathode and anode. Initially, lithium cobalt oxide was used as the cathode and polyacetylene as the anode. Later in 1985, it was found that using lithium cobalt oxide as the cathode and graphite as the anode produced an excellent secondary battery based on both enhanced battery stability and the frontier electron theory of Dr. Kenichi Fukui This enabled the development of portable equipment, such as cell phones and laptops. However, before lithium ion batteries could be mass produced for widespread use, safety concerns needed to be addressed such as overheating and over potential. One key to ensuring safety has been the use of a separator between the cathode and anode. This prevents physical contact between the two electrodes while still enabling ionic transport. Furthermore, Dr. Yoshino developed a microporous polyethylene membrane separator with a “fuse” function. In the case of abnormal heat generation within the battery cell, the separator provides a shutdown mechanism in which the micropores of the separator close by melting and the ionic flow instantly terminates. In 2004, a novel electroactive polymer separator with the function of overcharge protection was first proposed by Dr. Denton et al. This kind of separator can switch reversibly between insulating and conducting states in response of the changes in charge potential based on the intrinsic properties of the conducting polymer. Therefore, one can see how polymer separator's function and purpose has changed over time. Now, a separators primary function is to provide a protection mechanism for a battery while also effectively transporting ionic charge carriers between the two electrodes as well as preventing the electric contact between them.

Synthesis

Polymer separators generally fall in the category of microporous polymer membranes. Microporous polymer membranes are usually fabricated from a variety of inorganic, organic, and naturally occurring materials. The pore size in these types of polymer separators is typically larger than 50-100 Å. Materials such as nonwoven fibers (cotton, nylon, polyesters, glass), polymer films (polyethylene, polypropylene, poly (tetrafluoroethylene), poly (vinyl chloride), and naturally occurring substances (rubber, asbestos, wood). There are also ion exchange membranes which are fabricated from polymeric materials that have pores with diameters of less than 20 Å. These are not typically used in batteries because their pore size is too small. The methods for manufacturing the microporous membranes and ion exchange membranes can be divided into two processes: dry process and wet processes.

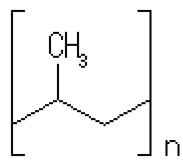
Dry Process

The dry process consists of three steps: extruding, annealing, and stretching. The extruding step is generally carried out at a temperature higher than the melting point of the polymer resin. This is because the polymer resins are melted in order to shape them into a uniaxially orientated tubular film, called a precursor film. The structure and orientation of the precursor film produced depends on the processing conditions and the characteristics of the polymer resin used. In the next step, the annealing process, the precursor polymer is annealed at a temperature slightly lower than the melting point of the polymer. The purpose of this step is to improve the crystalline structure in order to enable the formation of micropores in the final step, stretching. In the final step, stretching, the annealed film is deformed along the machine direction by a process consisting of a cold stretch, a hot stretch, and a relaxation. The cold stretch is used to create the pore structure by stretching the film at a lower temperature with a faster strain rate, and the hot stretch is to increase the size of the pores by further stretching the film at a higher temperature with a slower strain rate. The purpose of the relaxation step is to reduce internal stress within the film. The porosity of the final film depends on the morphology of the precursor film, annealing conditions, and the stretching ratios and conditions.

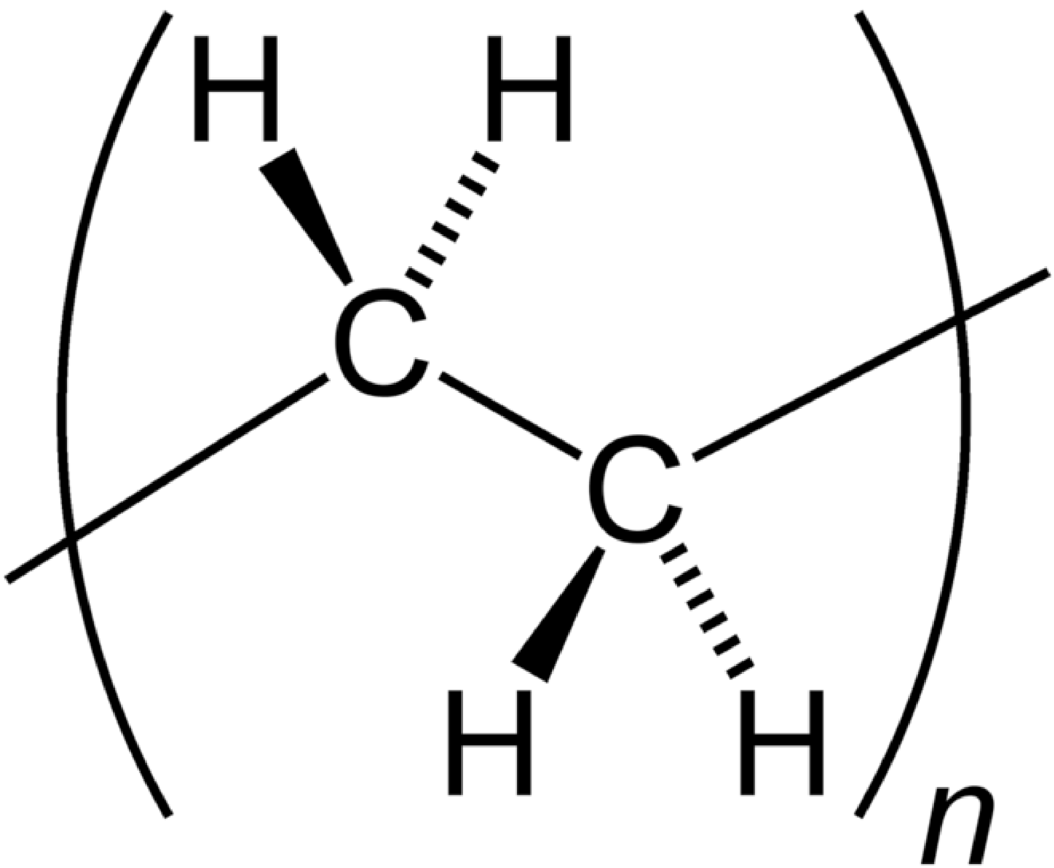
Wet Process

Similar to the dry process the wet process consists of three steps: the mixing of the polymer resins, paraffin oil, antioxidant and other additives and then heating to produce a homogenous solution, then forcing the heated solution through a sheet die into a gel-like film, and then finally extracting the paraffin oil and other additives with a volatile solvent to form the microporous structure.

Different types of polymers used in batteries



The chemical structure of polypropylene.



The chemical structure of polythylene.

There are specific types of polymers which are ideal for the different types of synthesis. Most of polymers currently used in battery separators are polyolefin based materials with semi-crystalline structure. Among them, polyethylene, polypropylene, and their blends such as polyethylene-polypropylene are widely used. Recently, graft polymers have been studied in an attempt to improve battery performance, including micro-porous poly(methyl methacrylate)-grafted and siloxane grafted polyethylene separators, which show favorable surface morphology and electrochemical properties as compared to conventional polyethylene separators. In addition, poly(vinylidene fluoride) (PVDF) nanofiber webs can be synthesized as a separator to improve both ion conductivity and dimensional stability Another type of polymer separator, polytriphenylamine (PTPAn)-modified separator, is an electroactive separator with reversible overcharge protection.

Ideal Polymers for Dry Processes

The dry process is only suitable for polymers with high crystallinity. These include but are not limited to: semi-crystalline polyolefins, polyoxymethylene, and isotactic poly (4-methyl-1-pentene). One can also use blends of two immiscible polymers, in which at least one polymer has a crystalline structure, such as polyethylene-polypropylene, polystyrene-polypropylene, and poly (ethylene terephthalate) - polypropylene blends.

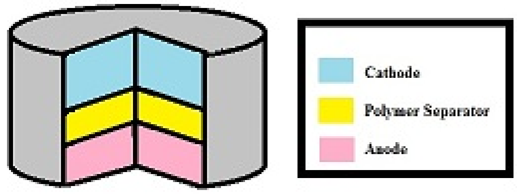
Ideal Polymers for Wet Processes

The wet process is suitable for both crystalline and amorphous polymers. The separators synthesized by wet processes often use ultrahigh-molecular-weight polyethylene. The use of these polymers enables the batteries to have favorable mechanical properties while also preventing the battery from functioning when it becomes too hot.

Wet process vs. Dry process

Membranes synthesized by dry processes are more suitable for a high power density battery because they have an open and uniform pore structure, while those made by wet processes are more suited for a long cycle life battery because of their tortuous and interconnected porous structure. This helps to suppress the growth of Li crystals on the graphite anode during fast charging or low temperature charging.

Placement of Polymer Separators in Batteries



Side view of a battery.

The separator is placed between the anode and the cathode. The pores of the separator are filled with the electrolyte. The electrode and separator combination is then wound into tight rolls which are then fitted into rigid cylindrical or prismatic (rectangular) metal cans.

Properties of Polymer Separators

Chemical Stability

The separator material must be chemically stable against the electrolyte and electrode materials, especially under the strongly reductive and oxidative environments when the battery is fully charged. The separator should not degrade and lose mechanical strength. One can determine the chemical stability of a polymer separator by calendar life testing.

Thickness of Separator

A battery separator must be relatively thin in order to facilitate the high energy and power densities of the battery. However, if the separator is too thin, it can decrease the mechanical strength and safety of the battery. Additionally, a separator should have uniform thickness in order to support the long like cycle of a battery. In current technologies, 25.4μm is generally accepted as the standard width. The thickness of a polymer separator can be measured using the T411 om-83 method developed under the auspices of the Technical Association of the Pulp and Paper Industry.

Porosity of Separator

The separator must have the correct amount of porosity in order to hold a sufficient amount of liquid electrolyte in order to enable the movement of ions between the electrodes. The porosity cannot be too high because this hinders the ability of the pores to close, which is a vital component of the separators ability to shut down a battery. The porosity can be measured using liquid or gas absorption methods according to the American Society for Testing and Materials (ASTM) D-2873. Typically, a Li-ion battery separator will have a porosity of 40%.

Pore Size

Pore size is also very important to the functioning of the separator. The pore size must be smaller than the particle size of the electrode components, including the electrode active materials and the conducting additives. Ideally the pores should be uniformly distributed while also having a tortuous structure. This ensures a uniform current distribution throughout the separator while suppressing the growth of Li on the anode. The distribution and structure of pores can be analyzed using a Capillary Flow Porometer or a Scanning Electron Microscope.

Permeability

The separator should not limit the electrical performance of the battery. Usually the presence of a polymer separator will increase the resistance of the electrolyte by a factor of four to five. The ratio of the resistance of the separator filled with electrolyte divided by the resistance of the electrolyte alone is called the MacMullin number. Air permeability can be used indirectly to estimate the MacMullin number. Air permeability is expressed in terms of the Gurley value, which is defined as the time required for a specific amount of air to pass through a specific area of the separator under a specific pressure. The Gurley value reflects the tortuosity of the pores, when the porosity and thickness of the separators are fixed. A separator with uniform porousness is vital to the long life cycle of a battery. Deviations from uniform permeability will result in uneven current density distribution, which causes the formation of Li crystals on the graphite anode.

Mechanical Strength

The separator must be strong enough to withstand the tension of the winding operation during battery assembly. The mechanical strength of the polymer separator is also very important. Mechanical strength is typically defined in terms of the tensile strength in two directions, the machine direction and the transverse direction, and terms of the tear resistance and puncture strength. All of these parameters are defined in terms of Young's modulus.

Wetability

The electrolyte must be able to fill the entire battery assembly therefore, it is important that the separator wet easily when submerged in the electrolyte. Furthermore, the separator should be able to retain the electrolyte permanently, which increases the cycle life of the battery. There is not a generally accepted method used to test wettability, other than placing a droplet of electrolyte onto the separator and observing what happens.

Stability

It is important that the separator remain stable over a wide temperature range. It is essential that once the separator is soaked with electrolyte it lays completely flat.

Thermal Capabilities

Another major requirement for separators in lithium-ion batteries is the ability to shut down at a temperature slightly lower than that at which thermal runaway occurs. Even though the separator must be able to shut down at particular temperatures, it must be able to retain its mechanical properties.

Defects

Many Structural defects can form in polymer separators due to temperature changes. These structural defects can result in a thicker separators. Furthermore, there can be intrinsic defects in the polymers themselves, such as polyethylene often begins to deteriorate during the stages of polymerization, transportation, and storage. Additionally, defects such as tears or holes can form during the synthesis of polymer separators. There are also other sources of defects can come from doping the polymer separator. Recently groups have been trying to improve the wetability of the polyer separators by co-dopping the normal polyethylene separator with acrylonitrile. The researchers found that acrylonitrile was more susceptible to be compatible with the electrolyte due to the wettability property.

Use in Li-ion Batteries

Polymer separators, similar to battery separators in general, act as a separator of the anode and cathode in the Li-ion battery while also enabling the movement of ions through the cell. Additionally, many of the polymer separators, typically multilayer polymer separators, can act as “shutdown separators”, which are able to shut down the battery if it becomes too hot during the cycling process. These multilayered polymer separators are generally composed of one or more polyethylene layers which serve to shut down the battery and at least one polypropylene layers which acts as a form of mechanical support for the separator.

Other types of battery separators

In addition to polymer separators, there are several other types of separators. There are nonwovens, which consist of a manufactured sheet, web, or matt of directionally or randomly oriented fibers. Supported liquid membranes, which consist of a solid and liquid phase contained within a microporous separator. Additionally there are also polymer electrolytes which can form complexes with different types of alkali metal salts, which results in the production of ionic conductors which serve as solid electrolytes. Another type of separator, a solid ion conductor, can serve as both a separator and the electrolyte in a battery.

Advancements in Polymer Separators

The topic of polymer separators has been an active area of research due to the application of lithium-ion batteries in full or hybrid electric vehicles. These types of vehicles need to have lithium-ion batteries that contain high energy and power density. In other words, if one were to accelerate a full electric vehicle the secondary cell needs to output a large amount of energy as quickly as possible. DupontTM has introduced a novel nano-fiber based polymeric battery separator that boosts the performance and safety of lithium-ion batteries. These types of separators, named EnergainTM, are potential candidates for use in full electric vehicles in the near future. The EnergainTM separators are synthesized into a web using a proprietary spinning process that creates continuous filaments. These filaments can range in diameter from 200 – 1,000 nanometers. The separators exhibit stability and low shrinkage in high temperatures and are easily saturated in common organic electrolytes. This results in more efficient operation, longer battery life, and improved safety. Batteries containing this type of separator can be quickly recharged, deliver improved performance, and reduce the number of cells needed by up to thirty-three percent for hybrid electric vehicles. Overall, this type of polymer separator can increase power up to thirty percent. Also, the battery life can also be increased by twenty percent. This is due to their stability at high temperatures and the overall morphology of the separator. With more battery power, drivers can travel farther on a single charge and accelerate more quickly and safely.

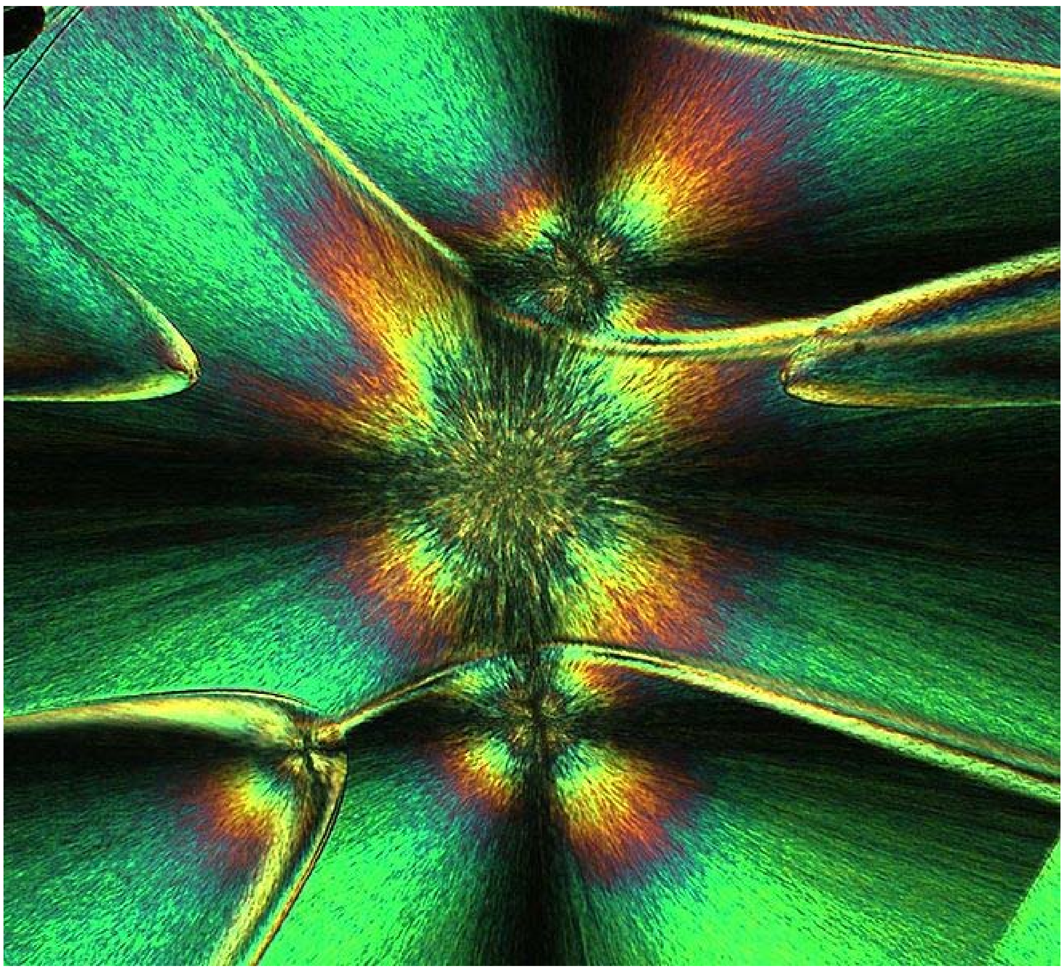
As seen previously, polymer separators are of great importance, especially in the area of lithium-ion batteries. Jun Young Kim at Massachusetts Institute of Technology used plasma technology to modify a polyethylene membrane to create a high performance separator for practical applications in rechargeable lithium ion polymer batteries. Plasma treatment methods have been developed to modify polymer surfaces for enhanced adhesion, wettability, and printability. These are usually performed by modifying the surfaces on only several molecular levels. This allows the surface functionalization of polymers without sacrificing the bulk properties. The surface of the polyethylene membrane was modified with acrylonitrile via plasma coating technique. The lithium-ion polymer cell that contained the plasma induced acrylonitrile coated polyethylene (PiAn-PE) membrane was analyzed using various spectroscopic techniques. The surface characterization demonstrated that the enhanced adhesion of PiAN-PE membrane resulted from the increased polar component of surface energy. The presence of PiAN induced onto the surface of PE membrane via plasma modification process plays a crucial role in improving the wettability and electrolyte retention, the interfacial adhesion between the electrodes and the separator, and the cycle performance of the resulting lithium-ion polymer cell assembly. This plasma-modified PE membrane holds a great potential to be a promising polymer membrane as a high-performance and cost-effective separator for lithium-ion polymer batteries. These polymer separators are also used in other secondary cells.

Another example of a secondary cell is the sealed rechargeable nickel/metal hydride battery. This offers significant improvement over conventional rechargeable batteries in terms of performance and environmental friendliness. The Ni/MH, like the lithium-ion battery, has the ability to display high energy and power density. These batteries have long cycle lives making them a leading technology as a battery source for electric vehicles. However, the greatest problem of Ni/MH cells are their inherent high corrosion rate in aqueous solutions. As a contribution to alkaline Ni/MH secondary battery technology, there has been a strong demand to replace the conventional aqueous electrolyte by a solid or gel polymer electrolyte/separator. In Ni/MH cells, the most commonly used separators are porous insulator films of polyolefin, nylon, or cellophane. Another way to modify these porous insulator films is the process of radiation grafting. Acrylic compounds can be radiation-grafted onto these separators to make their properties more desirable i.e. more wettable and permeable to the electrolyte. Zhijiang Cai and co-workers developed a solid polymer membrane gel separator. This was a polymerization product of one or more monomers selected from the group of water-soluble ethylenically unsaturated amides and acid. The polymer-based gel also includes a water swellable polymer, which acts as a reinforcing element. In addition, ionic species are added to the solution and remain embedded in the polymer gel after polymerization. Recently, more and more Ni/MH batteries of bipolar design are being developed because they offer some advantages for applications as high power storage systems for electric vehicles. It was found that this solid polymer membrane gel separator could be very useful for such applications in bipolar design. In other words, this design can help in avoiding short-circuits occurring in liquid-electrolyte systems.

Inorganic polymer separators have also been of interest as use in lithium-ion batteries. Inorganic particulate film/poly(methyl methacrylate) (PMMA)/inorganic particulate film trilayer separators are prepared by means of simple dip-coating of inorganic particle layers on to both sides of PMMA thin films. This inorganic trilayer membrane is believed to be an inexpensive, novel separator for application in lithium-ion batteries due to the increased dimensional and thermal stability.

Chapter 8

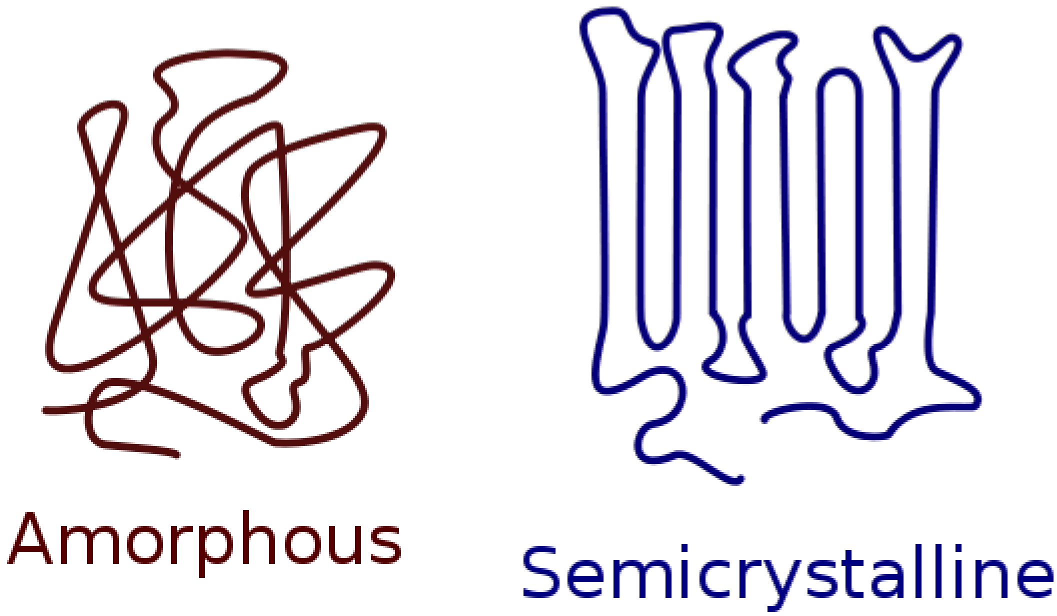
Crystallization of Polymers



Spherulites viewed between crossed polarizers in an optical microscope.

Crystallization of polymers is a process associated with partial alignment of their molecular chains. These chains fold together and form ordered regions called lamellae, which compose larger spheroidal structures named spherulites. Polymers can crystallize upon cooling from the melt, mechanical stretching or solvent evaporation. Crystallization affects optical, mechanical, thermal and chemical properties of the polymer. The degree of crystallinity is estimated by different analytical methods and it typically ranges between 10 and 80%, thus crystallized polymers are often called "semicrystalline". The properties of semicrystalline polymers are determined not only by the degree of crystallinity, but also by the size and orientation of the molecular chains.

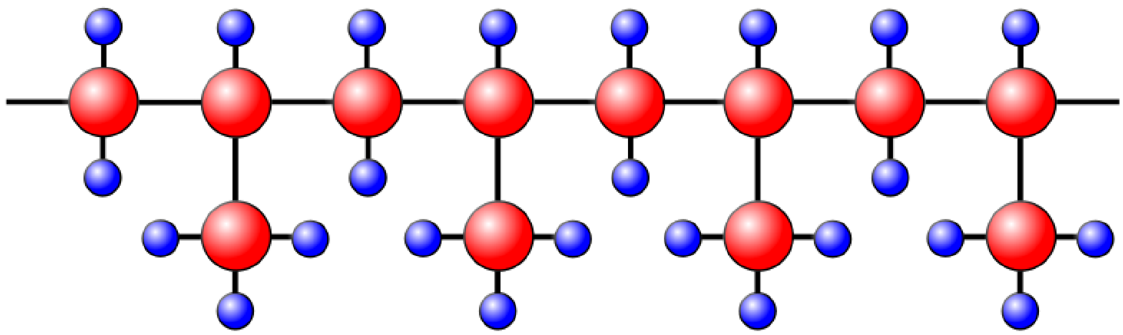
Crystallization mechanisms



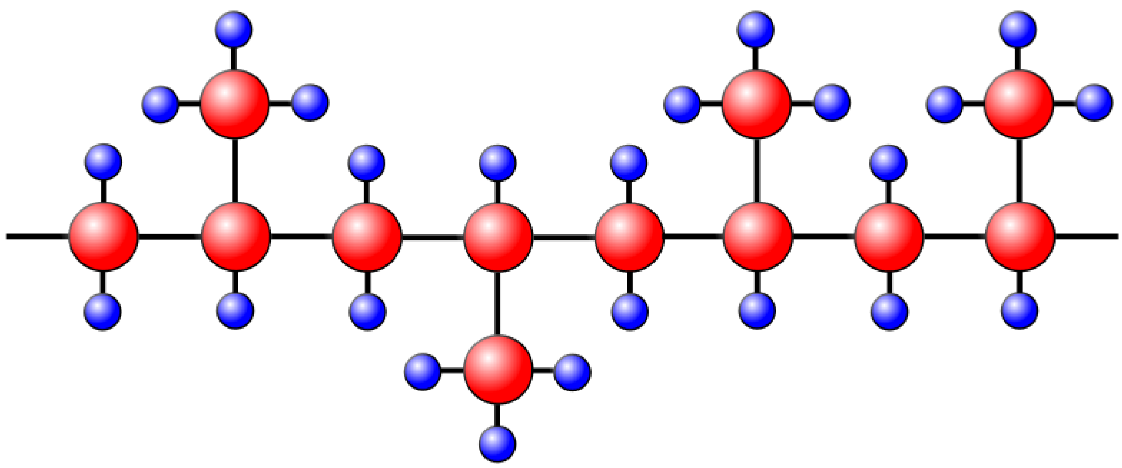
The arrangement of molecular chains in amorphous and semicrystalline polymers.

Solidification from the melt

Polymers are composed of long molecular chains which form irregular, entangled coils in the melt. Some polymers retain such a disordered structure upon freezing and thus convert into amorphous solids. In other polymers, the chains rearrange upon freezing and form partly ordered regions with a typical size of the order 1 micrometer. Although it would be energetically favorable for the polymer chains to align parallel, such alignment is hindered by the entanglement. Therefore, within the ordered regions, the polymer chains are both aligned and folded. Those regions are therefore are neither crystalline nor amorphous and are classified as semicrystalline. Examples of semi-crystalline polymers are linear polyethylene (PE), polyethylene terephthalate PET polytetrafluoroethylene (PTFE) or isotactic polypropylene (PP).



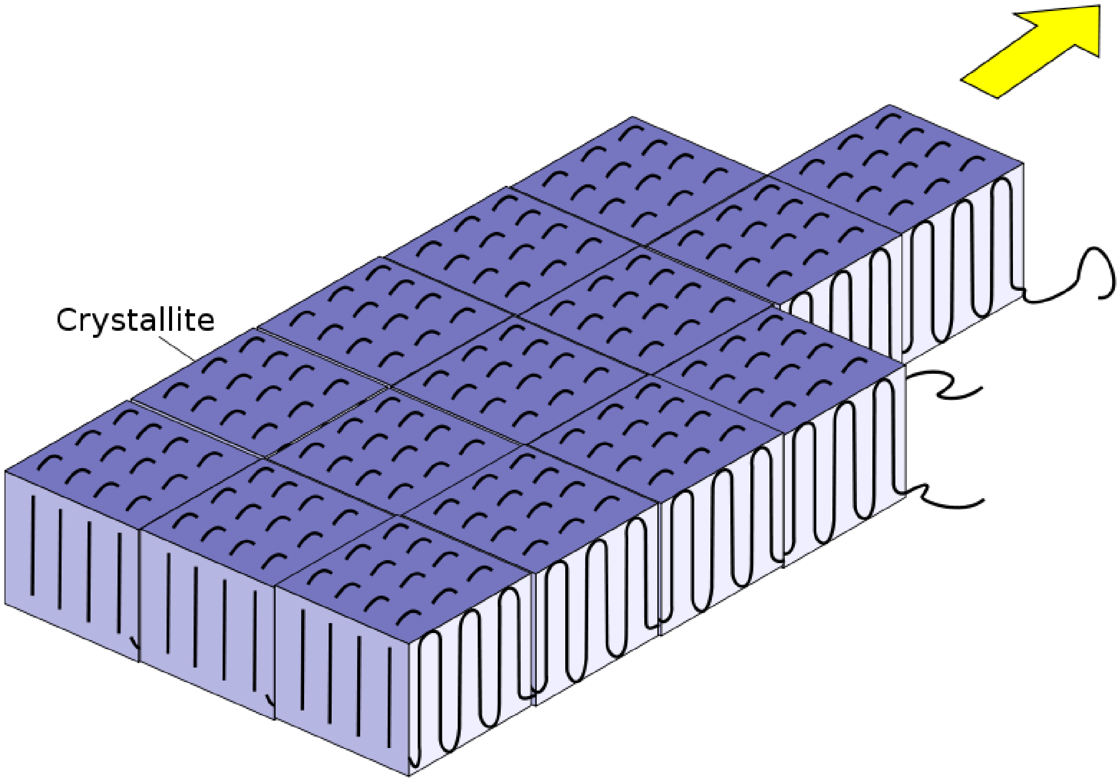
The structure of isotactic polypropylene.



The structure of atactic polypropylene.

Whether or not polymers can crystallize depends on their molecular structure – presence of straight chains with regularly spaced side groups facilitates crystallization. For example, crystallization occurs very much easier in isotactic than in the atactic polypropylene form. Atactic polymers crystallize when the side groups are very small, as in polyvinyl and don't crystallize in case of large substituents like in rubber or silicones.

Nucleation

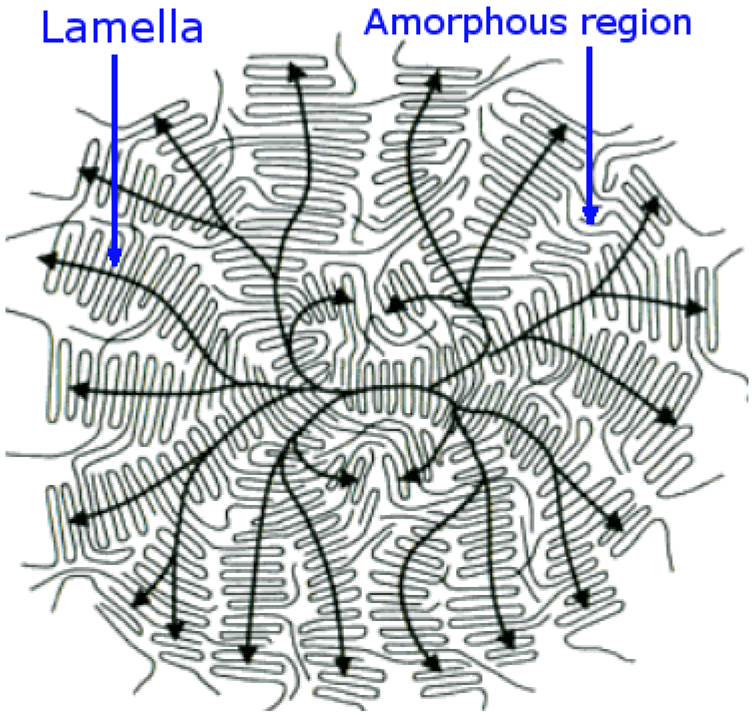


Lamellae form during crystallization from the melt. The arrow shows the direction of temperature gradient.

Nucleation starts with small, nanometer-sized areas where as a result of heat motion some chains or their segments occur parallel. Those seeds can either dissociate, if thermal motion destroys the molecular order, or grow further, if the grain size exceeds a certain critical value.

Apart from the thermal mechanism, nucleation is strongly affected by impurities, dyes, plasticizers, fillers and other additives in the polymer. This is also referred to as heterogeneous nucleation. This effect is poorly understood and irregular, so that the same additive can promote nucleation in one polymer, but not in another. Many of the good nucleating agents are metal salts of organic acids, which themselves are crystalline at the solidification temperature of the polymer solidification.

Crystal growth from the melt



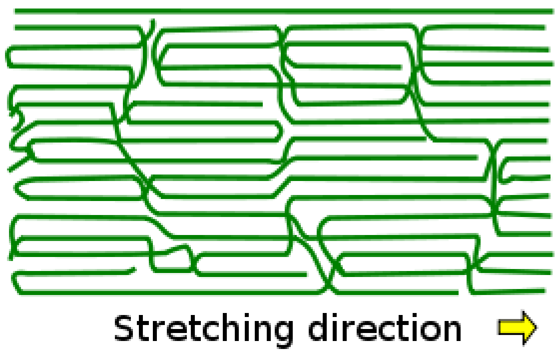
Schematic model of a spherulite. Black arrows indicate direction of molecular alignment

Crystal growth is achieved by the further addition of folded polymer chain segments and only occurs for temperatures below the melting temperature T_m and above the glass transition temperature T_g. Higher temperatures destroy the molecular arrangement and below the glass transition temperature, the movement of molecular chains is frozen. Nevertheless, secondary crystallization can proceeds even below T_g, in the time scale of months and years. This process affects mechanical properties of the polymers and decreases their volume because of a more compact packing of aligned polymer chains.

The chains interact via various types of the van der Waals forces. The interaction strength depends on the distance between the parallel chain segments and it determines the mechanical and thermal properties of the polymer.

The growth of the crystalline regions preferably occurs in the direction of the largest temperature gradient and is suppressed at the top and bottom of the lamellae by the amorphous folded parts at those surfaces. In case of strong gradient, the growth has a unidirectional, dendritic character. However, if temperature distribution is isotropic and static then lamellae grow radially and form larger quasi-spherical aggregated called spherulites. Spherulites have a size between about 1 and 100 micrometers and form a large variety of colored patterns (see, e.g. front images) when observed between crossed polarizers in an optical microscope, which often include the "maltese cross" pattern and other polarization phenomena caused by molecular aignment within the individual lamellae of a spherullite.

Crystallization by stretching



The arrangement of the molecule chains upon crystallization by stretching.

The above mechanism considered crystallization from the melt, which is important for injection molding of plastic components. Another type of crystallization occurs upon extrusion used in making fibers and films.

In this process, the polymer is forced through, e.g., a nozzle that creates tensile stress which partially aligns its molecules. Such alignment can be considered as crystallization and it affects the material properties. For example, the strength of the fiber is greatly increased in the longitudinal direction, and optical properties show large anisotropy along and perpendicular to the fiber axis. Polymer strength is increased not only by extrusion, but also by blow molding, which is used in the production of plastic tanks and PET bottles. Some polymers which do not crystallize from the melt, can be partially aligned by stretching.

Crystallization from solution

Polymers can also be crystallized from a solution or upon evaporation of a solvent. This process depends on the degree of dilution: in dilute solutions, the molecular chains have no connection with each other and exist as a separate polymer coils in the solution. Increase in concentration which can occur via solvent evaporation, induces interaction between molecular chains and a possible crystallization as in the crystallization from the melt. Crystallization from solution may results in the highest degree of polymer crystallinity. For example, highly linear polyethylene can form platelet-like single crystals with a thickness on the order 10–20 nm when crystallized from a dilute solution. The crystal shape can be more complex for other polymers, including hollow pyramids, spirals and multilayer dendritic structures.

A very different process is precipitation; it uses a solvent which dissolves individual monomers but not the resulting polymer. When a certain degree of polymerization is reached, the polymerized and partially crystallized product precipitates out of the solution. The rate of crystallization can be monitored by a technique which selectively probes the dissolved fraction, such as nuclear magnetic resonance.

Degree of crystallinity

The fraction of the ordered molecules in polymer is characterized by the degree of crystallinity, which typically ranges between 10 and 80%.Higher values are only achieved in materials having small molecules, which are usually brittle, or in samples stored for long time at temperatures just under the melting point. The latter procedure is costly and is applied only in special cases.

Most methods of evaluating the degree of crystallinity assume a mixture of perfect crystalline and totally disordered areas; the transition areas are expected to amount to several percent. These methods include density measurement, differential scanning calorimetry (DSC), X-ray diffraction (XRD), infrared spectroscopy and nuclear magnetic resonance (NMR). The measured value depends on the method used, which is therefore quoted together with the degree of crystallinity.

In addition to the above integral methods, the distribution of crystalline and amorphous regions can be visualized with microscopic techniques, such as polarized light microscopy and transmission electron microscopy).

Degree of crystallinity (D, %) and densities of crystalline (ρ_c) and amorphous (ρ_a, g/cm^3) polymers.

Polymer	**D**	ρ_c	ρ_a
Nylon (PA66 and PA6)	35–45	1.24	1.08
Polyoxymethylene (POM)	70–80	1.54	1.28
Polyethylene terephthalate (PET)	30–40	1.50	1.33
Polybutylene terephthalate (PBT)	40–50	–	–
Polytetrafluoroethylene (PTFE)	60–80	2.35	2.00
isotactic polypropylene	70–80	0.95	0.85
atactic polypropylene	~0	–	–
High-density polyethylene	70–80	1.0	0.85
Low-density polyethylene	45–55	1.0	0.85

Density measurements

Crystalline areas are generally more densely packed than amorphous areas. This results in a higher density, up to 15% depending on the material. For example, polyamide 6 (nylon) has crystalline density $\rho_c = 1.24$ g/cm^3 and amorphous density $\rho_a = 1.08$ g/cm^3). However, moisture which is often present in the sample does affect this type of measurement.

Calorimetry

Additional energy is released upon melting a semicrystalline polymer. This energy can be measured with differential scanning calorimetry and compared with that released upon melting of the standard sample of the same material with known crystallization degree.

X-ray diffraction

Regular arrangement of atoms and molecules produce sharp diffraction peaks whereas amorphous regions result in broad halos. The diffraction pattern of polymers usually contains a combination of both. Degree of crystallinity can be estimated by integrating the relative intensities of the peaks and halos.

Infrared spectroscopy (IR)

Infrared absorption or reflection spectra from crystalline polymers contain additional peaks which are absent in amorphous materials with the same composition. These signals may originate from deformation vibrations of the regular arrangement of molecular chains. From the analysis of these bands, the degree of crystallinity can be estimated.

Nuclear magnetic resonance (NMR)

crystalline and amorphous areas differ by the mobility of protons. The latter can be monitored through the line shape of NMR signals and used to estimate the degree of crystallinity.

Properties of semicrystalline polymers

Thermal and mechanical properties

Below their glass transition temperature, amorphous polymers are usually hard and brittle because of the low mobility of their molecules. Increasing the temperature induces molecular motion resulting in the typical rubber-elastic properties. A constant force applied to a polymer at temperatures above T_g results in a viscoelastic deformation, i.e., the polymer begins to creep. Heat resistance is thus given for amorphous polymers just below the glass transition temperature.

Relatively strong intermolecular forces in semicrystalline polymers prevent softening even above the glass transition temperature. Their elastic modulus changes significantly only at high (melting) temperature.It also depends on the degree of crystallinity: higher crystallinity results in a harder and more thermally stable, but also more brittle material, whereas the amorphous regions provide certain elasticity and impact resistance. Another characteristic feature of semicrystalline polymers is strong anisotropy of their mechanical properties along the direction of molecular alignment and perpendicular to it.

Plastics are viscoelastic materials meaning that under applied stress, their deformation increases with time (creep). The elastic properties of plastics are therefore distinguished according to the time scale of the testing to short-time behavior (such as tensile test which lasts minutes), shock loading, the behavior under long-term and static loading, as well as the vibration-induced stress.

Optical properties

Semicrystalline polymers are usually opaque because of light scattering on the numerous boundaries between the crystalline and amorphous regions. The density of such boundaries is lower and thus the transparency is higher either for low (amorphous polymer) or high (crystalline) degree of crystallinity. For example, atactic polypropylene is usually amorphous and transparent while syndiotactic polypropylene, which has crystallinity ~50%, is opaque. Crystallinity also affects dyeing of polymers: crystalline polymers are more difficult to stain than amorphous ones because the dye molecules penetrate much easier through amorphous regions.

Chapter 9

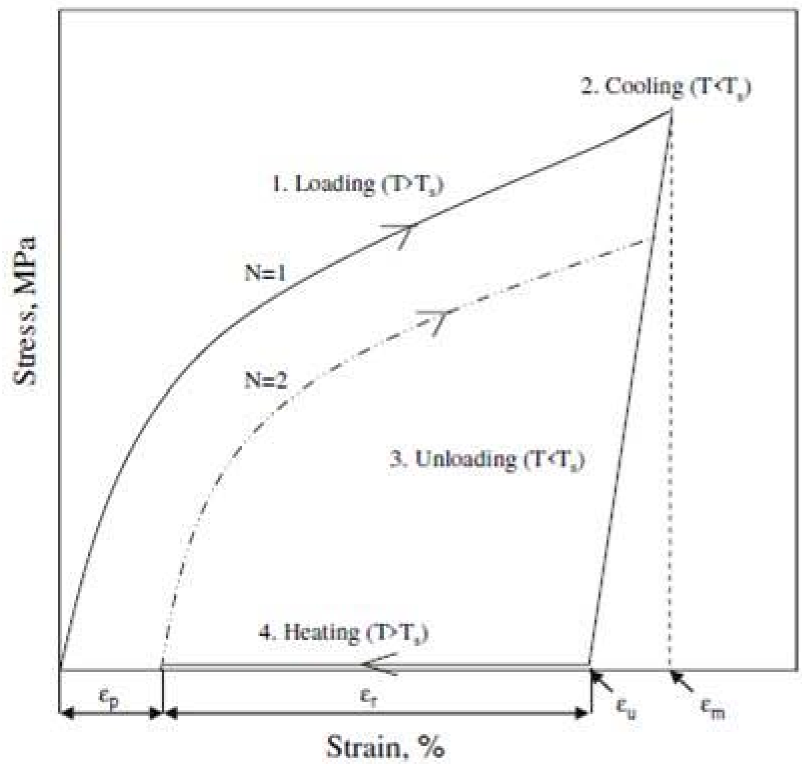
Shape Memory Polymer

Shape memory polymers (SMPs) are polymeric smart materials that have the ability to return from a deformed state (temporary shape) to their original (permanent) shape induced by an external stimulus (trigger), such as temperature change.

Properties of shape memory polymers

Most SMPs can retain two shapes, and the transition between those is induced by temperature. In some recent SMPs, heating to certain transition temperatures allows to fix three different shapes. In addition to temperature change, the shape change of SMPs can also be triggered by an electric or magnetic field, light or solution. As well as polymers in general, SMPs also cover a wide property-range from stable to biodegradable, from soft to hard, and from elastic to rigid, depending on the structural units that constitute the SMP. SMPs include thermoplastic and thermoset (covalently cross-linked) polymeric materials. SMPs are known to be able to store up to three different shapes in memory.

Two important quantities that are used to describe shape memory effects are the strain recovery rate (R_r) and strain fixity rate (R_f). The strain recovery rate describes the ability of the material to memorize its permanent shape, while the strain fixity rate describes the ability of switching segments to fix the mechanical deformation.



Result of the cyclic thermomechanical test

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$
$$R_f(N) = \frac{\varepsilon_p(N)}{\varepsilon_m}$$

where N is the cycle number, ε_m is the maximum strain imposed on the material, and $\varepsilon_p(N)$ and $\varepsilon_p(N\text{-}1)$ are the strains of the sample in two successive cycles in the stress-free state before yield stress is applied.

Shape memory effect can be described briefly as the following mathematical model:

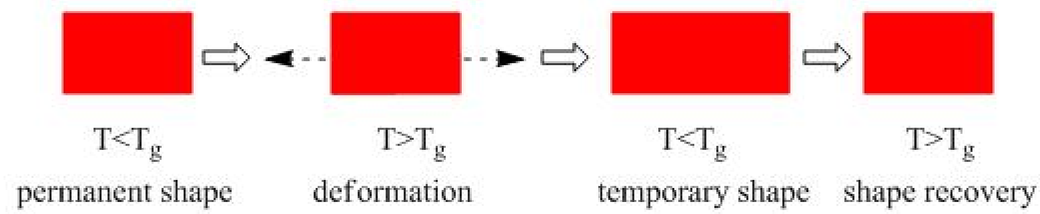
$$R_f(N) = 1 - \frac{E_f}{E_g}$$
$$R_r(N) = 1 - \frac{f_I R}{f_\alpha(1 - E_f/E_g)}$$

where E_g is the glassy modulus, E_r is the rubbery modulus, f_{IR} is viscous flow strain and f_α is strain for $t >> t_r$.

Triple-Shape Memory

While most traditional shape-memory polymers can only hold a permanent and temporary shape, recent technological advances have allowed the introduction of triple-shape memory materials. Much as a traditional two-shape memory polymer will change from a temporary shape back to a permanent shape at a particular temperature, triple-shape memory polymers will switch from one temporary shape to another at the first transition temperature, and then back to the permanent shape at another, higher activation temperature. This is usually achieved by combining two double-shape memory polymers with different glass transition temperatures.

Description of the thermally induced shape memory effect



A schematic representation of the shape memory effect

Polymers exhibiting a shape memory effect have both a visible, current (temporary) form and a stored (permanent) form. Once the latter has been manufactured by conventional methods, the material is changed into another, temporary form by processing through heating, deformation, and finally, cooling. The polymer maintains this temporary shape until the shape change into the permanent form is activated by a predetermined external stimulus. The secret behind these materials lies in their molecular network structure, which contains at least two separate phases. The phase showing the highest thermal transition, T_{perm}, is the temperature that must be exceeded to establish the physical crosslinks responsible for the permanent shape. The switching segments, on the other hand, are the segments with the ability to soften past a certain transition temperature (T_{trans}) and are responsible for the temporary shape. In some cases this is the glass transition temperature (T_g) and others the melting temperature (T_m). Exceeding T_{trans} (while remaining below T_{perm}) activates the switching by softening these switching segments and thereby allowing the material to resume its original (permanent) form. Below T_{trans}, flexibility of the segments is at least partly limited. If T_m is chosen for programming the SMP, strain-induced crystallization of the switching segment can be initiated when it is stretched above T_m and subsequently cooled below T_m These crystallites form covalent netpoints which prevent the polymer from reforming its usual coiled structure. The hard to soft segment ratio is often between 5/95 and 95/5, but ideally this ratio is between 20/80 and 80/20. The shape memory polymers are effectively viscoelastic and many models and analysis methods exist.

Thermodynamics of the shape memory effect

In the amorphous state, polymer chains assume a completely random distribution within the matrix. W represents the probability of a strongly coiled conformation, which is the conformation with maximum entropy, and is the most likely state for an amorphous linear polymer chain. This relationship is represented mathematically as $k = \ln W$, where k is the Boltzmann constant.

In the transition from the glassy state to a rubber-elastic state by thermal activation, the rotations around segment bonds become increasingly unimpeded. This allows chains to assume other possibly, energetically equivalent conformations with a small amount of disentangling. As a result, the majority of SMPs will form compact, random coils because this conformation is entropically favored over a stretched conformation.

Polymers in this elastic state with number average molecular weight greater than 20,000 stretch in the direction of an applied external force. If the force is applied for a short time, the entanglement of polymer chains with their neighbors will prevent large movement of the chain and the sample recovers its original conformation upon removal of the force. If the force is applied for a longer period of time, however, a relaxation process takes place whereby a plastic, irreversible deformation of the sample takes place due to the slipping and disentangling of the polymer chains.

To prevent the slipping and flow of polymer chains, cross-linking can be used, both chemical and physical.

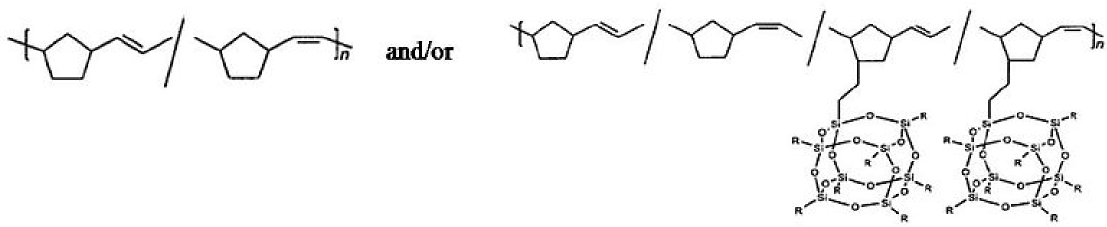
Physically crosslinked SMPs

Linear block copolymers

Representative shape memory polymers in this category are polyurethanes, polyurethanes with ionic or mesogenic components made by prepolymer method. Other block copolymers also show the shape memory effect, such as, block copolymer of polyethylene terephthalate (PET) and polyethyleneoxide (PEO), block copolymers containing polystyrene and poly(1,4-butadiene), and an ABA triblock copolymer made from poly(2-methyl-2-oxazoline) and polytetrahydrofuran.

Other thermoplastic polymers

A linear, amorphous polynorbornene (Norsorex, developed by CdF Chemie/Nippon Zeon) or organic-inorganic hybrid polymers consisting of polynorbornene units that are partially substituted by polyhedral oligosilsesquioxane (POSS) also have shape memory effect.



R = Cyclopentyl or cyclohexyl

Chemically crosslinked SMPs

The main limitation of physically crosslinked polymers for the shape memory application is irreversible deformation during memory programming due to the creep. The network polymer can be synthesized by either polymerization with multifunctional (3 or more) crosslinker or by subsequent crosslinking of a linear or branched polymer. They form insoluble materials which swell in certain solvents.

Crosslinked polyurethane

This material can be made by using excess diisocyanate or by using a crosslinker such as glycerin, trimethylol propane. Introduction of covalent crosslinking improves in creep, increase in recovery temperature and recovery window.

PEO based crosslinked SMPs

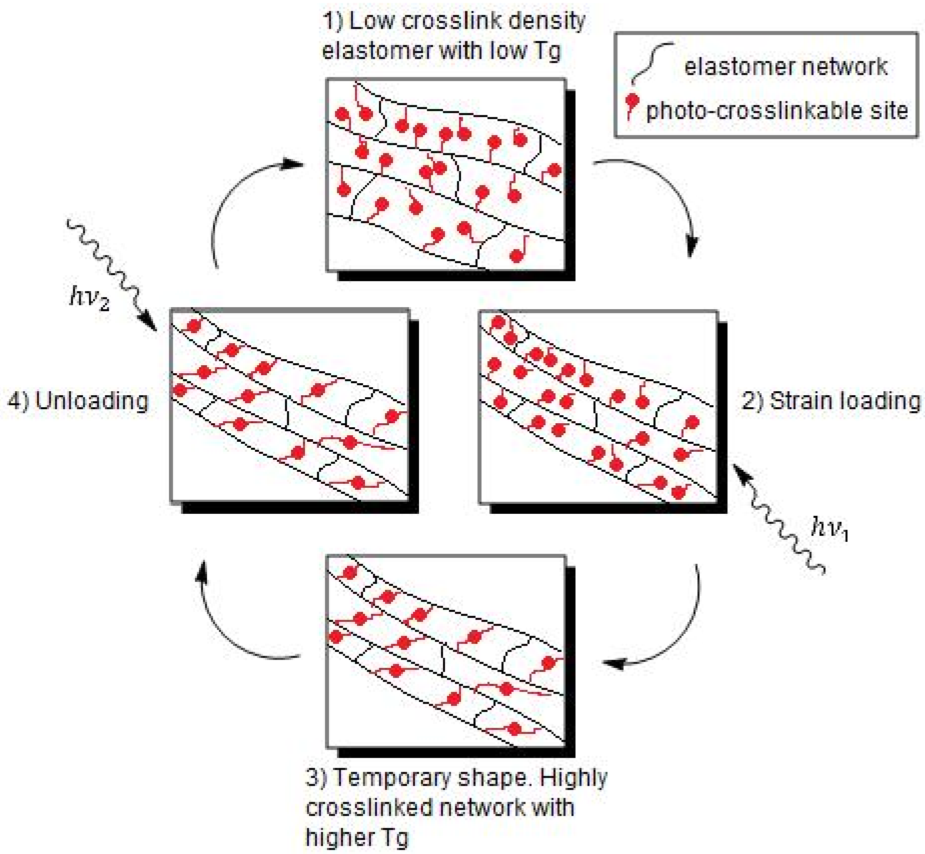
The PEO-PET block copolymers can be crosslinked by using maleic anhydride, glycerin or dimethyl 5-isopthalates as a crosslinking agent. The addition of 1.5 wt% maleic anhydride increased in shape recovery from 35% to 65% and tensile strength from 3 to 5 MPa.

Hard phase	Crosslinker	T_r (°C)	R_f(5)(%)	R_f(5)(%)
PET	Glycerol/dimethyl 5-sulfoisopthalate	11–30	90–95	60–70
PET	Maleic anhydride	8–13	91–93	60
AA/MAA copolymer	N,N'-methylene-bis-acrylamide	90		99
MAA/N-vinyl-2-pyrrolidone	Ethyleneglycol dimethacrylate	90		99
PMMA/N-vinyl-2-pyrrolidone	Ethyleneglycol dimethacrylate	45, 100		99

Thermoplastic Shape-Memory

While shape memory effects are traditionally limited to thermosetting plastics, recent developments in technology have allowed the use of some thermoplastic polymers, most notably PEEK, in shape memory applications.

Light-induced SMPs



A schematic representation of reversible LASMP crosslinking

Light activated shape memory polymers (LASMP) use processes of photo-crosslinking and photo-cleaving to change T_g. Photo-crosslinking is achieved by using one wavelength of light, while a second wavelength of light reversibly cleaves the photo-crosslinked bonds. The effect achieved is that the material may be reversibly switched between an elastomer and a rigid polymer. Light does not change the temperature, only the cross-linking density within the material. For example, it has been reported that polymers containing cinnamic groups can be fixed into predetermined shapes by UV light illumination (> 260 nm) and then recover their original shape when exposed to UV light of a different wavelength (< 260 nm). Examples of photoresponsive switches include cinnamic acid and cinnamylidene acetic acid.

Electro-active SMPs

The use of electricity to activate the shape memory effect of polymers is desirable for applications where it would not be possible to use heat and is another active area of research. Some current efforts use conducting SMP composites with carbon nanotubes. short carbon fibers (SCFs). carbon black, metallic Ni powder. These conducting SMPs are produced by chemically surface-modifying multi-walled carbon nanotubes (MWNTs) in a mixed solvent of nitric acid and sulfuric acid, with the purpose of improving the interfacial bonding between the polymers and the conductive fillers. The shape memory effect in these types of SMPs have been shown to be dependent on the filler content and the degree of surface modification of the MWNTs, with the surface modified versions exhibiting good energy conversion efficiency and improved mechanical properties.

Another technique being investigated involves the use of surface-modified super-paramagnetic nanoparticles. When introduced into the polymer matrix, remote actuation of shape transitions is possible. An example of this involves the use of oligo (e-capolactone)dimethacrylate/butyl acrylate composite with between 2 and 12% magnetite nanoparticles. Nickel and hybrid fibers have also been used with some degree of success.

Shape memory polymers vs. shape memory alloys

A summary of the major differences between SMPs and SMAs

	SMPs	SMAs
Density (g/cm^3)	0.9–1.1	6–8
Extent of deformation	up to 800%	<8%
Required stress for deformation (MPa)	1–3	50–200
Stress generated upon recovery (MPa)	1–3	150–300
Transition temperatures (°C)	–10..100	–10..100
Recovery speed	1s – minutes	<1s
Processing conditions	<200 °C low pressure	>1000 °C high pressure
Costs	<$10/lb	~$250/lb

Shape memory polymers differ from shape memory alloys by their glass transition or melting transition from a hard to a soft phase which is responsible for the shape memory effect. In shape memory alloys martensitic/austenitic transitions are responsible for the shape memory effect. There are numerous advantages that make SMPs more attractive than shape memory alloys. They have a high capacity for elastic deformation (up to 200% in most cases), much lower cost, lower density, a broad range of application temperatures which can be tailored, easy processing, and potential biocompatibility and biodegradability.

Applications

Industrial applications

One of the first conceived industrial applications was in robotics where shape memory (SM) foams were used to provide initial soft pretension in gripping. These SM foams could be subsequently hardened by cooling making a shape adaptive grip. Since this time the materials have seen widespread usage in e.g. the building industry (foam which expands with warmth to seal window frames), sports wear (helmets, judo and karate suits) and in some cases with thermochromic additives for ease of thermal profile observation. Polyurethane SMPs are also applied as an autochoke element for engines.

Medical applications

Most medical applications of SMP have yet to be developed, but devices with SMP are now beginning to hit the market. Recently, this technology has expanded to applications in orthopedic surgery, such as the Morphix suture anchor and ExoShape graft fixation device, by MedShape Solutions.

Potential medical applications

SMPs are smart materials with potential applications as, e.g., intravenous cannula, self-adjusting orthodontic wires and selectively pliable tools for small scale surgical procedures where currently metal-based shape memory alloys such as Nitinol are widely used. Another application of SMP in the medical field could be its use in implants: for example minimally invasive, trough small incisions or natural orifices, implantation of a device in its small temporary shape. Shape memory technologies have shown great promise for cardiovascular stents, since they allow a small stent to be inserted along a vein or artery and then expanded to prop it open. After activating the shape memory by temperature increase or mechanical stress, it would assume its permanent shape. Certain classes of shape memory polymers possess an additional property: biodegradability. This offers the option to develop temporary implants. In the case of biodegradable polymers, after the implant has fulfilled its intended use, e.g. healing/tissue regeneration has occurred, the material degrades into substances which can be eliminated by the body. Thus full functionality would be restored without the necessity for a second surgery to remove the implant (to avoid inflammation). Examples of this development are vascular stents and surgical sutures. When used in surgical sutures, the shape memory property of SMPs enables wound closure with self-adjusting optimal tension, which avoids tissue damage due to overtightened sutures and does support healing and regeneration.

Potential industrial applications

Further potential applications include self-repairing structural components, such as e.g. automobile fenders in which dents are repaired by application of temperature. After an undesired deformation, such as a dent in the fender, these materials "remember" their original shape. Heating them activates their "memory." In the example of the dent, the fender could be repaired with a heat source, such as a hair-dryer. The impact results in a temporary form, which changes back to the original form upon heating—in effect, the plastic repairs itself. SMPs may also be useful in the production of aircraft which would morph during flight. Currently, the Defense Advanced Research Projects Agency DARPA is testing wings which would change shape by 150%.

Other potential applications

Some of the various other applications of SMPs include clothing. For example, a shirt could be programmed to shorten sleeves or increase the pore size of the clothing as temperature increases to increase breathability of the fabric and therefore regulate body temperature by increased ability of heat and water vapor to escape.

Chapter 10

Thermoplastic Elastomer

Thermoplastic elastomers (**TPE**), sometimes referred to as **thermoplastic rubbers**, are a class of copolymers or a physical mix of polymers (usually a plastic and a rubber) which consist of materials with both thermoplastic and elastomeric properties. While most elastomers are thermosets, thermoplastics are in contrast relatively easy to use in manufacturing, for example, by injection molding. Thermoplastic elastomers show both advantages typical of rubbery materials and plastic materials. The principal difference between thermoset elastomers and thermoplastic elastomers is the type of crosslinking bond in their structures. In fact, crosslinking is a critical structural factor which contributes to impart high elastic properties. The crosslink in thermoset polymers is a covalent bond created during the vulcanization process. On the other hand the crosslink in thermoplastic elastomer polymers is a weaker dipole or hydrogen bond or takes place in one of the phases of the material.

Types

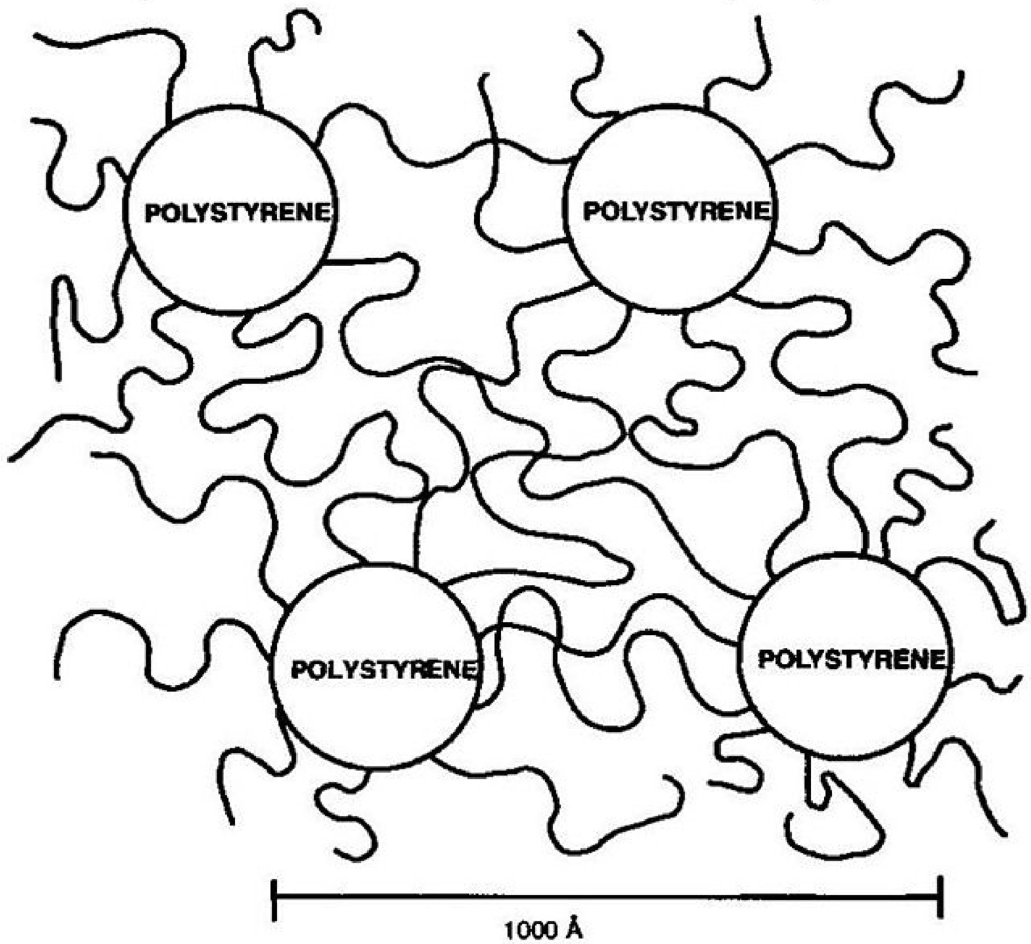
Thermoplastic polyurethanes

There are six generic classes of TPEs generally considered to exist commercially. They are styrenic block copolymers, polyolefin blends, elastomeric alloys (TPE-v or TPV), thermoplastic polyurethanes, thermoplastic copolyester and thermoplastic polyamides. Examples of TPE products that come from block copolymers group are Arnitel (DSM), Engage (Dow chemical), Hytrel (Du Pont), Kraton (Shell chemicals), Pebax (Arkema), Pellethane, Riteflex (Ticona), Styroflex (BASF) and more. While there are now many commercial products of elastomer alloy, these include: Alcryn (Du Pont), Dryflex, Evoprene (AlphaGary), Forprene, Geolast (Monsanto), Mediprene, Santoprene and Sarlink (DSM).

In order to qualify as a thermoplastic elastomer, a material must have these three essential characteristics:

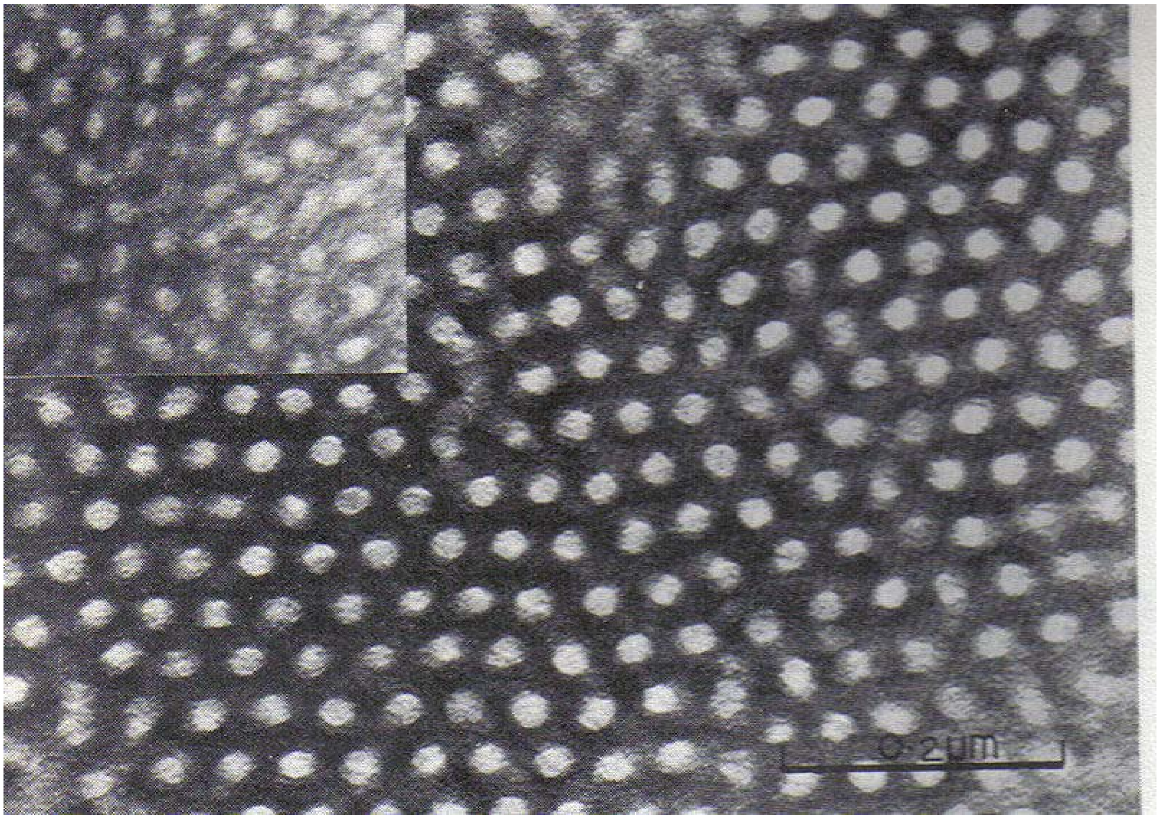
1. The ability to be stretched to moderate elongations and, upon the removal of stress, return to something close to its original shape.
2. Processable as a melt at elevated temperature.
3. Absence of significant creep.

Background



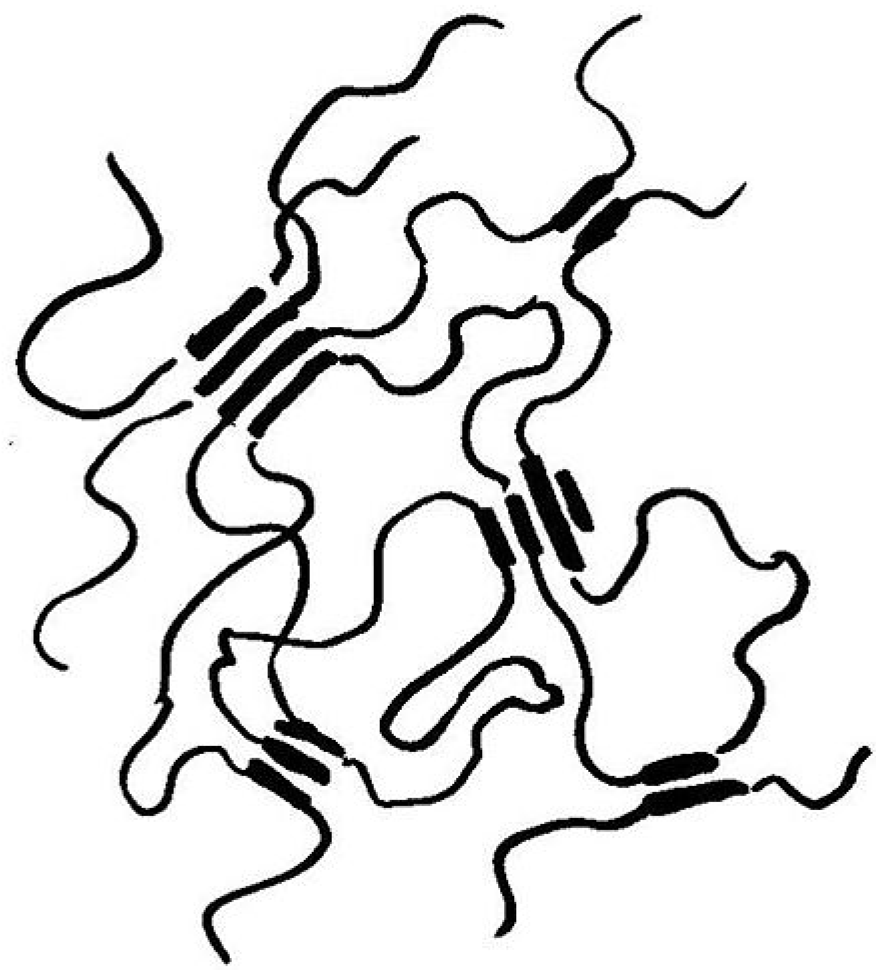
SBS block copolymer schematic microstructure

It was not until the 1950s, when thermoplastic polyurethane polymers became available, that TPE became a commercial reality. During the 1960s styrene block copolymer became available, and in the 1970s a wide range of TPEs came on the scene. The worldwide usage of TPEs (680,000 tons/year in 1990) is growing at about 9% per year. The styrene-butadiene materials possess a two-phase microstructure due to incompatibility between the polystyrene and polybutadiene blocks, the former separating into spheres or rods depending on the exact composition. With low polystyrene content, the material is elastomeric with the properties of the polybutadiene predominating. Generally they offer a much wider range of properties than conventional cross-linked rubbers because the composition can varies to suit customer needs.



SBS block copolymer in TEM

Block copolymers are interesting because they can "microphase separate" to form periodic nanostructures, as in the styrene-butadiene-styrene block copolymer shown at right. The polymer is known as Kraton and is used for shoe soles and adhesives. Owing to the microfine structure, the transmission electron microscope or TEM was needed to examine the structure. The butadiene matrix was stained with osmium tetroxide to provide contrast in the image. The material was made by living polymerization so that the blocks are almost monodisperse, so helping to create a very regular microstructure. The molecular weight of the polystyrene blocks in the main picture is 102,000; the inset picture has a molecular weight of 91,000, producing slightly smaller domains. The spacing between domains has been confirmed by small-angle X-ray scattering, a technique which gives information about microstructure. Since most polymers are incompatible with one another, forming a block polymer will usually result in phase separation, and the principle has been widely exploited since the introduction of the SBS block polymers, especially where one of the block is highly crystalline. One exception to the rule of incompatibility is the material Noryl, where polystyrene and polyphenylene oxide or PPO form a continuous blend with one another.



Schematic crystalline block copolymer

Other TPE's have crystalline domains where one kind of block co-crystallizes with other block in adjacent chains, such as in copolyester rubbers, achieving the same effect as in the SBS block polymers. Depending on the block length, the domains are generally more stable than the latter owing to the higher crystal melting point. That point determines the processing temperatures needed to shape the material, as well as the ultimate service use temperatures of the product. Such materials include Hytrel, a polyester-polyether copolymer and Pebax, a nylon or polyamide-polyether copolymer.

Advantages

TPE materials have the potential to be recyclable since they can be molded, extruded and reused like plastics, but they have typical elastic properties of rubbers which are not recyclable owing to their thermosetting characteristics. TPE also require little or no compounding, with no need to add reinforcing agents, stabilizers or cure systems. Hence, batch-to-batch variations in weighting and metering components are absent, leading to improved consistency in both raw materials and fabricated articles. TPEs can be easily colored by most types of dyes. Besides that, it consumes less energy and closer and more economical control of product quality is possible.

Disadvantages

The disadvantages of TPEs relative to conventional rubber or thermoset are relatively high cost of raw materials, general inability to load TPEs with low cost fillers such as carbon black (therefore preventing TPEs from being used in automobile tires), poor chemical and heat resistance, high compression set and low thermal stability. TPEs soften or melt at elevated temperature above which they lose their rubbery behaviour. TPEs show creep behaviour on extended use.

Processing

The two most important manufacturing methods with TPEs are extrusion and injection molding. Compression molding is seldom, if ever, used. Fabrication via injection molding is extremely rapid and highly economical. Both the equipment and methods normally used for the extrusion or injection molding of a conventional thermoplastic are generally suitable for TPEs. TPEs can also be processed by blow molding, thermoforming and heat welding.

Applications

TPEs are used where conventional elastomers cannot provide the range of physical properties needed in the product. These materials find large application in the automotive sector and in household appliances sector. Thus copolyester TPEs are used in snowmobile tracks where stiffness and abrasion resistance is at a premium. They are also widely used for catheters where nylon block copolymers offer a range of softness ideal for patients. Thermoplastic silicon and olefin blends are used for extrusion of glass run and dynamic weatherstripping car profiles. Styrene block copolymers are used in shoe soles for their ease of processing, and widely as adhesives. TPE is commonly used to make suspension bushings for automotive performance applications because of its greater resistance to deformation when compared to regular rubber bushings. TPE is also finding more and more uses as an electrical cable jacket/inner insulation.

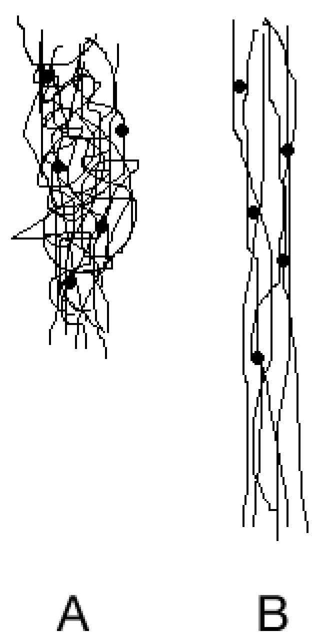
Chapter 11

Elastomer and Blow Molding

Elastomer

An **elastomer** is a polymer with the property of viscoelasticity (colloquially "elasticity"), generally having notably low Young's modulus and high yield strain compared with other materials. The term, which is derived from *elastic polymer*, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanisates. Each of the monomers which link to form the polymer is usually made of carbon, hydrogen, oxygen and/or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft (E~3MPa) and deformable. Their primary uses are for seals, adhesives and molded flexible parts.

Background



(A) is an unstressed polymer; (B) is the same polymer under stress. When the stress is removed, it will return to the A configuration. (The dots represent cross-links)

Elastomers are usually thermosets (requiring vulcanization) but may also be thermoplastic. The long polymer chains cross-link during curing, i.e., vulcanizing. The molecular structure of elastomers can be imagined as a 'spaghetti and meatball' structure, with the meatballs signifying cross-links. The elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibility, elastomers can reversibly extend from 5-700%, depending on the specific material. Without the cross-linkages or with short, uneasily reconfigured chains, the applied stress would result in a permanent deformation.

Temperature effects are also present in the demonstrated elasticity of a polymer. Elastomers that have cooled to a glassy or crystalline phase will have less mobile chains, and consequentially less elasticity, than those manipulated at temperatures higher than the glass transition temperature of the polymer.

It is also possible for a polymer to exhibit elasticity that is not due to covalent cross-links, but instead for thermodynamic reasons.

Examples of elastomers

Unsaturated rubbers that can be cured by sulfur vulcanization:

- Natural polyisoprene: cis-1,4-polyisoprene natural rubber (NR) and trans-1,4-polyisoprene gutta-percha
- Synthetic polyisoprene (IR for Isoprene Rubber)
- Polybutadiene (BR for Butadiene Rubber)
- Chloroprene rubber (CR), polychloroprene, Neoprene, Baypren etc.
- Butyl rubber (copolymer of isobutylene and isoprene, IIR)
    - Halogenated butyl rubbers (chloro butyl rubber: CIIR; bromo butyl rubber: BIIR)

- Styrene-butadiene Rubber (copolymer of styrene and butadiene, SBR)
- Nitrile rubber (copolymer of butadiene and acrylonitrile, NBR), also called Buna N rubbers
    - Hydrogenated Nitrile Rubbers (HNBR) Therban and Zetpol

(Unsaturated rubbers can also be cured by non-sulfur vulcanization if desired).

Saturated rubbers that cannot be cured by sulfur vulcanization:

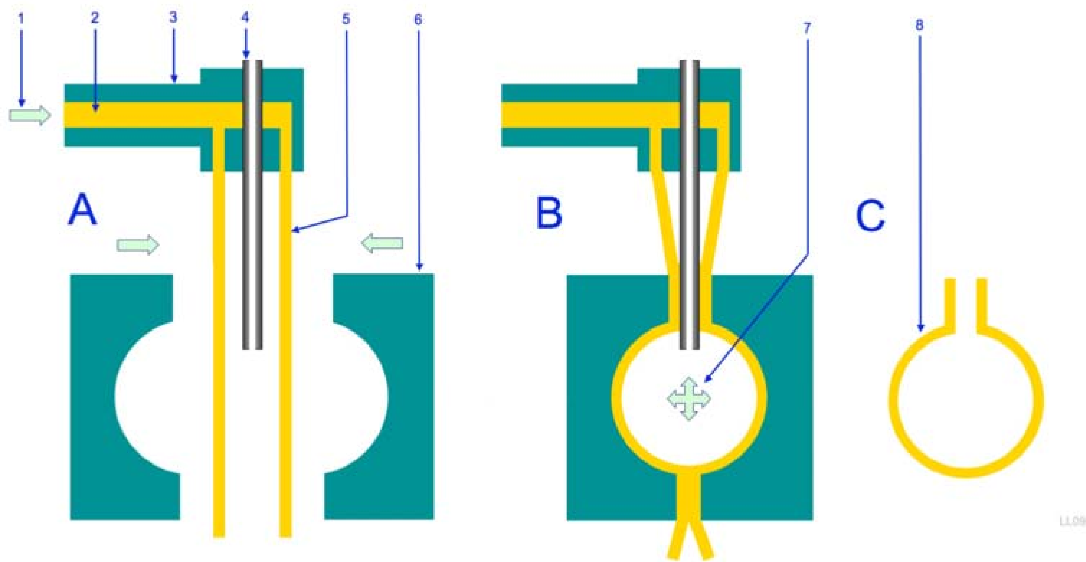
- EPM (**ethylene propylene rubber**, a copolymer of ethylene and propylene) and EPDM rubber (**ethylene propylene diene rubber**, a terpolymer of ethylene, propylene and a diene-component)
- Epichlorohydrin rubber (ECO)
- Polyacrylic rubber (ACM, ABR)
- Silicone rubber (SI, Q, VMQ)

- Fluorosilicone Rubber (FVMQ)
- Fluoroelastomers (FKM, and FEPM) Viton, Tecnoflon, Fluorel, Aflas and Dai-El
- Perfluoroelastomers (FFKM) Tecnoflon PFR, Kalrez, Chemraz, Perlast
- Polyether block amides (PEBA)
- Chlorosulfonated polyethylene (CSM), (Hypalon)
- Ethylene-vinyl acetate (EVA)

Various other types of elastomers:

- Thermoplastic elastomers (TPE)
- The proteins resilin and elastin
- Polysulfide rubber

Blow molding



The blow molding process

Blow molding (also known as **blow moulding** or **blow forming**) is a manufacturing process by which hollow plastic parts are formed. In general, there are three main types of blow molding: extrusion blow molding, injection blow molding, and stretch blow molding. The blow molding process begins with melting down the plastic and forming it into a parison or preform. The parison is a tube-like piece of plastic with a hole in one end in which compressed air can pass through.

The parison is then clamped into a mold and air is pumped into it. The air pressure then pushes the plastic out to match the mold. Once the plastic has cooled and hardened the mold opens up and the part is ejected.

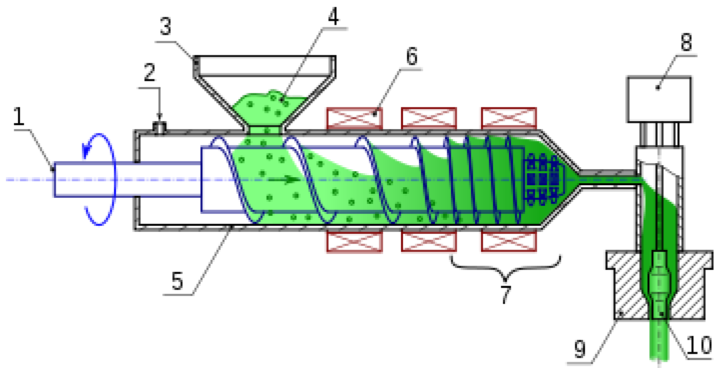
History of blow molding

There has been evidence found suggesting that Egyptians and Babylonians blew plastic materials, but Enoch Ferngren and William Kopitke were the first verified people who used the Blow Molding Process. The process principle comes from the idea of blowing glass. Ferngren and Kopitke produced a blow molding machine and sold it to Hartford Empire Company in 1937. This was the beginning of the commercial blow molding process. During the 1940s the variety and amount of products were still very limited and therefore blow molding did not take off until later. Once the variety and production rates went up the amount of products created followed soon there after. In the United States soft drink industry the amount of plastic containers went from zero in 1977 to ten Billion in 1999. Today even a greater amount of products are blown and it is expected to keep increasing.

For amorphous metals, also known as bulk metallic glasses (BMGs), blow molding has been recently demonstrated under pressures and temperatures comparable to plastic blow molding. This technique allows molding BMGs with an about 50 times higher strength than plastics into shapes that were previously not achievable with crystalline metals.

Typologies of blow molding

Extrusion blow molding



Extrusion blow molding

In **extrusion blow molding** (EBM), plastic is melted and extruded into a hollow tube (a parison). This parison is then captured by closing it into a cooled metal mold. Air is then blown into the parison, inflating it into the shape of the hollow bottle, container or part. After the plastic has cooled sufficiently, the mold is opened and the part is ejected. Continuous and Intermittent are two variations of Extrusion Blow Molding. In Continuous Extrusion Blow Molding the parison is extruded continuously and the individual parts are cut off by a suitable knife. In Intermittent blow molding there are two processes: straight intermittent is similar to injection molding whereby the screw turns, then stops and pushes the melt out. With the accumulator method, an accumulator gathers melted plastic and when the previous mold has cooled and enough plastic has accumulated, a rod pushes the melted plastic and forms the parison. In this case the screw may turn continuously or intermittently.

EBM processes may be either continuous (constant extrusion of the parison) or intermittent. Types of EBM equipment may be categorized as follows:

Continuous extrusion equipment

- rotary wheel blow molding systems
- shuttle machinery

Intermittent extrusion machinery

- reciprocating screw machinery
- accumulator head machinery

Examples of parts made by the EBM process include dairy containers, shampoo bottles, hoses/pipes, and hollow industrial parts such as drums.

Injection blow molding

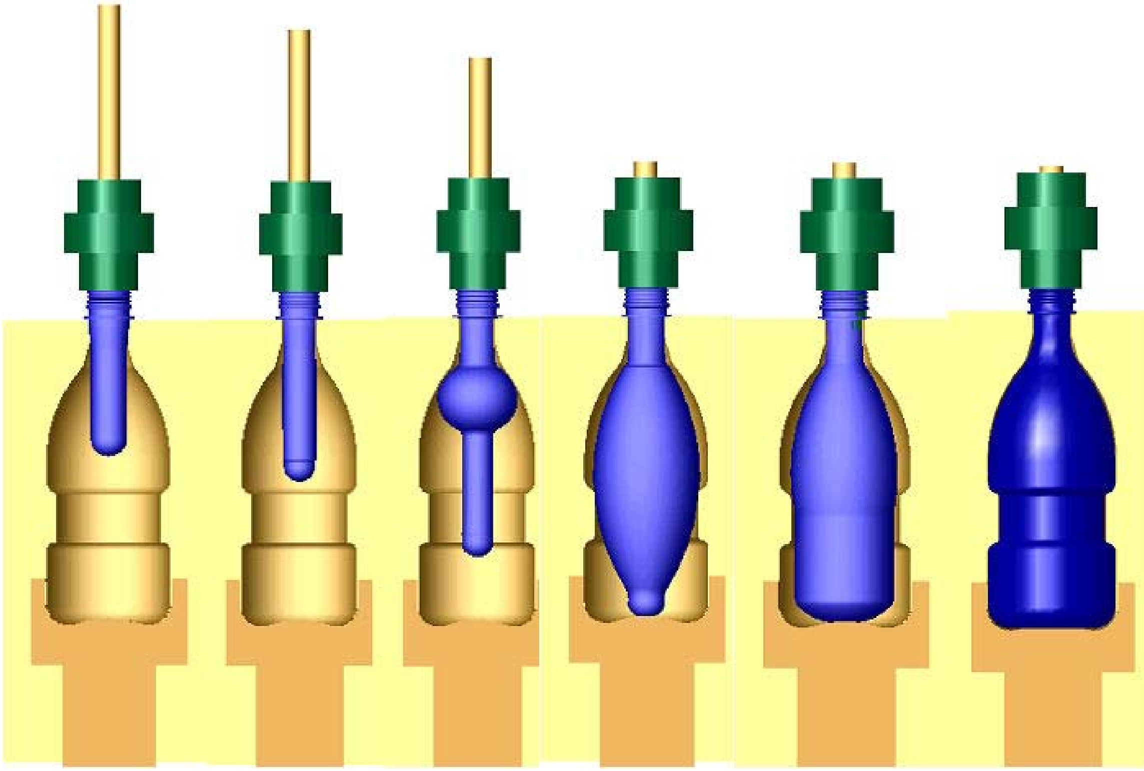
The process of **injection blow molding** (IBM) is used for the production of hollow glass and plastic objects in large quantities. In the IBM process, the polymer is injection molded onto a core pin; then the core pin is rotated to a blow molding station to be inflated and cooled. This is the least-used of the three blow molding processes, and is typically used to make small medical and single serve bottles. The process is divided into three steps: injection, blowing and ejection.

The injection blow molding machine is based on an extruder barrel and screw assembly which melts the polymer. The molten polymer is fed into a manifold where it is injected through nozzles into a hollow, heated preform mold. The preform mold forms the external shape and is clamped around a mandrel (the core rod) which forms the internal shape of the preform. The preform consists of a fully formed bottle/jar neck with a thick tube of polymer attached, which will form the body.

The preform mold opens and the core rod is rotated and clamped into the hollow, chilled blow mold. The core rod opens and allows compressed air into the preform, which inflates it to the finished article shape.

After a cooling period the blow mold opens and the core rod is rotated to the ejection position. The finished article is stripped off the core rod and leak-tested prior to packing. The preform and blow mold can have many cavities, typically three to sixteen depending on the article size and the required output. There are three sets of core rods, which allow concurrent preform injection, blow molding and ejection.

Stretch blow molding



Stretch blow molding process

In the **stretch blow molding** (SBM) process, the plastic is first molded into a "preform" using the injection molding process. These preforms are produced with the necks of the bottles, including threads (the "finish") on one end. These preforms are packaged, and fed later (after cooling) into a reheat stretch blow molding machine. In the SBM process, the preforms are heated (typically using infrared heaters) above their glass transition temperature, then blown using high pressure air into bottles using metal blow molds. Usually the preform is stretched with a core rod as part of the process. In the single-stage process both preform manufacture and bottle blowing are performed in the same machine. The stretching of some polymers, such as PET (polyethylene terephthalate) results in strain hardening of the resin, allowing the bottles to resist deforming under the pressures formed by carbonated beverages, which typically approach 60 psi.The main applications are bottles, jars and other containers.

Advantages of blow molding include: low tool and die cost; fast production rates; ability to mold complex part; produces recyclable parts

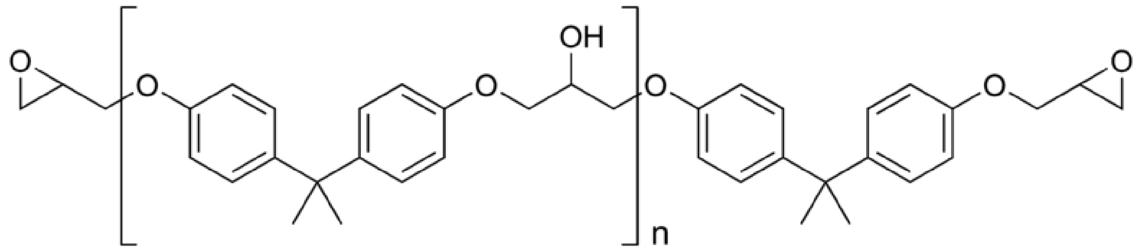
Chapter 12

Epoxy

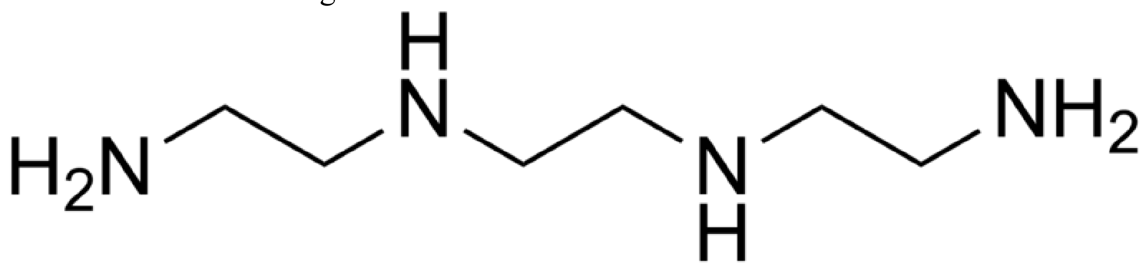
A syringe of "5-minute" epoxy

Epoxy or **polyepoxide** is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives.

Chemistry



Structure of unmodified epoxy prepolymer resin. *n* denotes the number of polymerized subunits and is in the range from 0 to about 25



Structure of TETA, a typical hardener. The amine (NH) groups react with the epoxide groups of the resin during polymerization.

Epoxy is a copolymer; that is, it is formed from two different chemicals. These are referred to as the "resin" and the "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end. Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals. The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked, and is thus rigid and strong.

The process of polymerization is called "curing", and can be controlled through temperature, choice of resin and hardener compounds, and the ratio of said compounds; the process can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time, and ambient temperatures.

History

The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the advanced materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now Hexion, formerly Resolution Polymers and others).

Applications

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allows cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified (for example silver-filled epoxies with good electrical conductivity are available, although epoxies are typically electrically insulating). Variations offering high thermal insulation, or thermal conductivity combined with high electrical resistance for electronics applications, are available.

Paints and coatings

Two part epoxy coatings were developed for heavy duty service on metal substrates and use less energy than heat-cured powder coatings. These systems use a 4:1 by volume mixing ratio, and dry quickly providing a tough, protective coating with excellent hardness. Their low volatility and water clean up makes them useful for factory cast iron, cast steel, cast aluminum applications and reduces exposure and flammability issues associated with solvent-borne coatings. They are usually used in industrial and automotive applications since they are more heat resistant than latex-based and alkyd-based paints. Epoxy paints tend to deteriorate, known as chalk out, due to UV exposure.

Polyester epoxies are used as powder coatings for washers, driers and other "white goods". Fusion Bonded Epoxy Powder Coatings (FBE) are extensively used for corrosion protection of steel pipes and fittings used in the oil and gas industry, potable water transmission pipelines (steel), concrete reinforcing rebar, *et cetera*. Epoxy coatings are also widely used as primers to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Metal cans and containers are often coated with epoxy to prevent rusting, especially for foods like tomatoes that are acidic. Epoxy resins are also used for high performance and decorative flooring applications especially terrazzo flooring, chip flooring and colored aggregate flooring.

Adhesives

Special epoxy is strong enough to withstand the forces between a surfboard fin and the fin mount. This epoxy is waterproof and capable of curing underwater. The blue-coloured epoxy on the left is still undergoing curing.

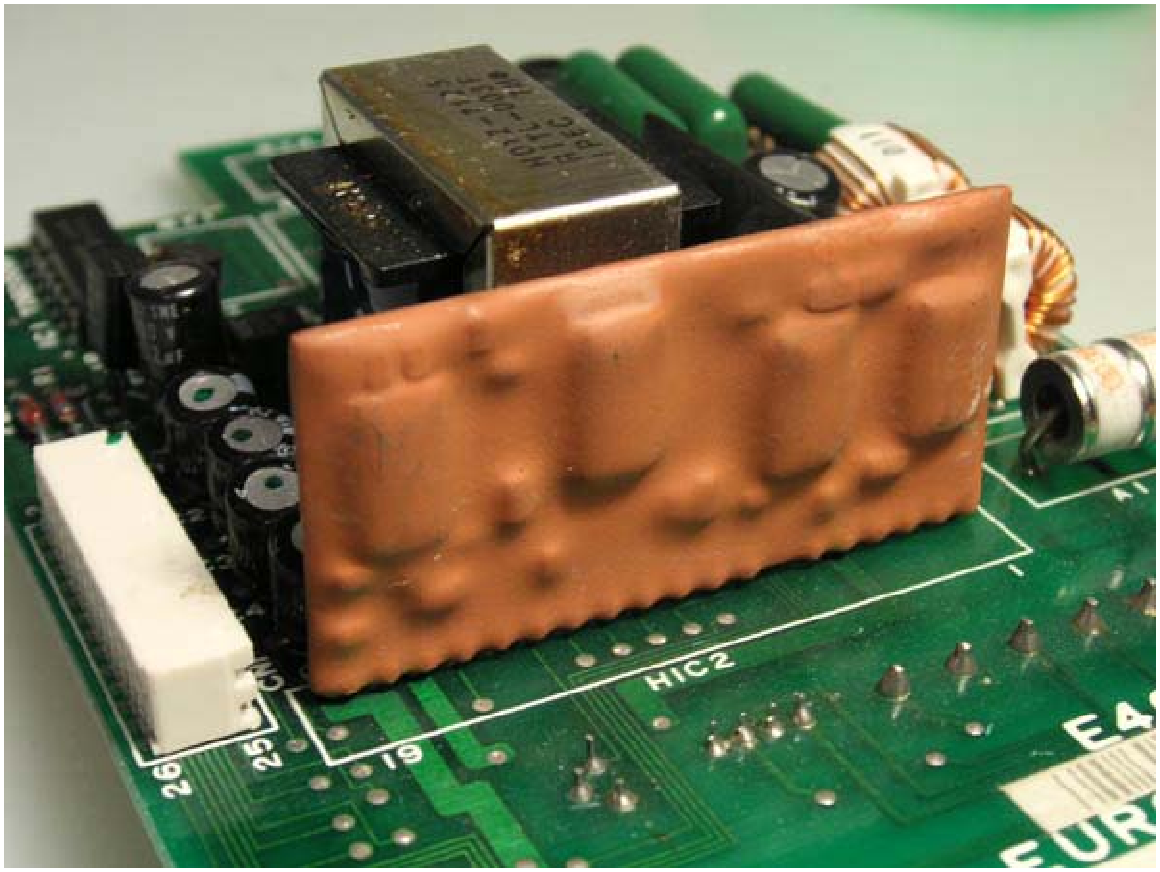
Epoxy adhesives are a major part of the class of adhesives called "structural adhesives" or "engineering adhesives" (that includes polyurethane, acrylic, cyanoacrylate, and other chemistries.) These high-performance adhesives are used in the construction of aircraft, automobiles, bicycles, boats, golf clubs, skis, snowboards, and other applications where high strength bonds are required. Epoxy adhesives can be developed to suit almost any application. They can be used as adhesives for wood, metal, glass, stone, and some plastics. They can be made flexible or rigid, transparent or opaque/colored, fast setting or slow setting. Epoxy adhesives are better in heat and chemical resistance than other common adhesives. In general, epoxy adhesives cured with heat will be more heat- and chemical-resistant than those cured at room temperature. The strength of epoxy adhesives is degraded at temperatures above 350 °F (177 °C).

Some epoxies are cured by exposure to ultraviolet light. Such epoxies are commonly used in optics, fiber optics, optoelectronics, and dentistry.

Industrial tooling and composites

Epoxy systems are used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids. This "plastic tooling" replaces metal, wood and other traditional materials, and generally improves the efficiency and either lowers the overall cost or shortens the lead-time for many industrial processes. Epoxies are also used in producing fiber-reinforced or composite parts. They are more expensive than polyester resins and vinyl ester resins, but usually produce stronger and more temperature-resistant composite parts.

Electrical systems and electronics



An epoxy encapsulated hybrid circuit on a printed circuit board.

Epoxy resin formulations are important in the electronics industry, and are employed in motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, dust and moisture. In the electronics industry epoxy resins are the primary resin used in overmolding integrated circuits, transistors and hybrid circuits, and making printed circuit boards. The largest volume type of circuit board—an "FR-4 board"—is a sandwich of layers of glass cloth bonded into a composite by an epoxy resin. Epoxy resins are used to bond copper foil to circuit board substrates, and are a component of the solder mask on many circuit boards.

Flexible epoxy resins are used for potting transformers and inductors. By using vacuum impregnation on uncured epoxy, winding-to-winding, winding-to-core, and winding-to-insulator air voids are eliminated. The cured epoxy is an electrical insulator and a much better conductor of heat than air. Transformer and inductor hot spots are greatly reduced, giving the component a stable and longer life than unpotted product.

Epoxy resins are applied using the technology of resin dispensing.

Consumer and marine applications

Epoxies are sold in hardware stores, typically as a pack containing separate resin and hardener, which must be mixed immediately before use. They are also sold in boat shops as repair resins for marine applications. Epoxies typically are not used in the outer layer of a boat because they deteriorate by exposure to UV light. They are often used during boat repair and assembly, and then over-coated with conventional or two-part polyurethane paint or marine-varnishes that provide UV protection.

There are two main areas of marine use. Because of the better mechanical properties relative to the more common polyester resins, epoxies are used for commercial manufacture of components where a high strength/weight ratio is required. The second area is that their strength, gap filling properties and excellent adhesion to many materials including timber have created a boom in amateur building projects including aircraft and boats.

Normal gelcoat formulated for use with polyester resins and vinylester resins does not adhere to epoxy surfaces, though epoxy adheres very well if applied to polyester resin surfaces. "Flocoat" that is normally used to coat the interior of polyester fibreglass yachts is also compatible with epoxies.

Epoxy materials tend to harden somewhat more gradually, while polyester materials tend to harden quickly, particularly if a lot of catalyst is used. The chemical reactions in both cases are exothermic. Large quantities of mix will generate their own heat and greatly speed the reaction, so it is usual to mix small amounts which can be used quickly.

While it is common to associate polyester resins and epoxy resins, their properties are sufficiently different that they are properly treated as distinct materials. Polyester resins are typically low strength unless used with a reinforcing material like glass fibre, are relatively brittle unless reinforced, and have low adhesion. Epoxies, by contrast, are inherently strong, somewhat flexible and have excellent adhesion. However, polyester resins are much cheaper.

Epoxy resins typically require a precise mix of two components which form a third chemical. Depending on the properties required, the ratio may be anything from 1:1 or over 10:1, but in every case they must be mixed exactly. The final product is then a precise thermo-setting plastic. Until they are mixed the two elements are relatively inert, although the 'hardeners' tend to be more chemically active and should be protected from the atmosphere and moisture. The rate of the reaction can be changed by using different hardeners, which may change the nature of the final product, or by controlling the temperature.

By contrast, polyester resins are usually made available in a 'promoted' form, such that the progress of previously-mixed resins from liquid to solid is already underway, albeit very slowly. The only variable available to the user is to change the rate of this process using a catalyst, often Methyl-Ethyl-Ketone-Peroxide (MEKP), which is very toxic. The presence of the catalyst in the final product actually detracts from the desirable properties, so that small amounts of catalyst are preferable, so long as the hardening proceeds at an acceptable pace. The rate of cure of polyesters can therefore be controlled both by the amount of catalyst and by the temperature.

As adhesives, epoxies bond in three ways: a) Mechanically, because the bonding surfaces are roughened; b) By proximity, because the cured resins are physically so close to the bonding surfaces that they are hard to separate; c) Ionically, because the epoxy resins form ionic bonds at an atomic level with the bonding surfaces. This last is substantially the strongest of the three. By contrast, polyester resins can only bond using the first two of these, which greatly reduces their utility as adhesives and in marine repair.

Aerospace applications

In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include glass, carbon, Kevlar, and boron. Epoxies are also used as a structural glue. Materials like wood, and others that are 'low-tech' are glued with epoxy resin.

Art

Epoxy resin, mixed with pigment, is used as a painting medium, by pouring layers on top of each other to form a complete picture.

Wind Energy applications

Epoxy resin is used in manufacturing the rotor blades of wind turbines. The resin is infused in the core materials, such as balsa wood or foam, and the reinforcing media, such as fabric, glass fibre or carbon fibre. The process is called VARTM, i.e. Vacuum Assisted Resin Transfer Moulding. Due to excellent properties and good finish, epoxy is the most favoured resin for composites.

Industry

As of 2006, the epoxy industry amounts to more than US$5 billion in North America and about US$15 billion worldwide. The Chinese market has been growing rapidly, and accounts for more than 30% of the total worldwide market. It is made up of approximately 50–100 manufacturers of basic or commodity epoxy resins and hardeners of which the three largest are Hexion (formerly Resolution Performance Products, formerly Shell Development Company; whose epoxy tradename is "Epon"), the Dow Chemical Company (tradename "D.E.R."), and Huntsman Corporation's Advanced Materials business unit (formerly Vantico, formerly Ciba Specialty Chemical; tradename "Araldite"). In 2007 Huntsman Corporation agreed to merge with Hexion (owned by the Apollo Group). KUKDO Chemical is one of the largest epoxy manufacturers in Asia, and recently their capacity has been increased up to 210,000 MT/Y (Korea 150,000 MT/Y, China 60,000 MT/Y and will be increased totally 300,000 MT/Y by 2009). Nanya Plastic also has the capacity of over 250,000 MT/Y (Taiwan and China), which is mostly for captive use. There are over 50 smaller epoxy manufacturers primarily producing epoxies only regionally, epoxy hardeners only, specialty epoxies, or epoxy modifiers.

These commodity epoxy manufacturers mentioned above typically do not sell epoxy resins in a form usable to smaller end users, so there is another group of companies that purchase epoxy raw materials from the major producers and then compounds (blends, modifies, or otherwise customizes) epoxy systems from these raw materials. These companies are known as "formulators". The majority of the epoxy systems sold are produced by these formulators and they comprise over 60% of the dollar value of the epoxy market. There are hundreds of ways that these formulators can modify epoxies—by adding mineral fillers (talc, silica, alumina, etc.), by adding flexibilizers, viscosity reducers, colorants, thickeners, accelerators, adhesion promoters, etc.. These modifications are made to reduce costs, to improve performance, and to improve processing convenience. As a result a typical formulator sells dozens or even thousands of formulations—each tailored to the requirements of a particular application or market.

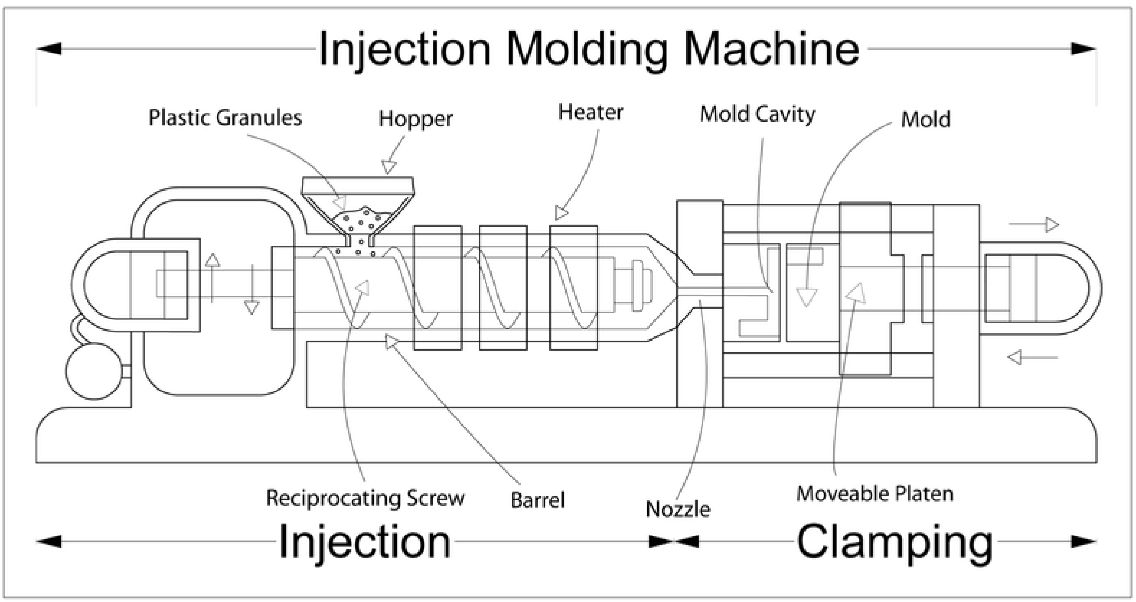
Impacted by the global economic slump, the epoxy market size declined to $15.8 billion in 2009, almost to the level of 2005. In some regional markets it even decreased nearly 20%. The current epoxy market is experiencing positive growth as the global economy revives. With an annual growth rate of 3.5 - 4% the epoxy market is expected to reach $17.7 billion by 2012 and $21.35 by 2015. Higher growth rate is foreseen thereafter due to stronger demands from epoxy composite market and epoxy adhesive market.

Health risks

The primary risk associated with epoxy use is sensitization to the hardener, which, over time, can induce an allergic reaction. It is a main source of occupational asthma among users of plastics. Bisphenol A, which is used in epoxy resin, is a known endocrine disruptor.

Chapter 13

Injection Molding



An injection molding machine

Injection molding (British English: **moulding**) is a manufacturing process for producing parts from both thermoplastic and thermosetting plastic materials. Material is fed into a heated barrel, mixed, and forced into a mold cavity where it cools and hardens to the configuration of the mold cavity. After a product is designed, usually by an industrial designer or an engineer, molds are made by a moldmaker (or toolmaker) from metal, usually either steel or aluminum, and precision-machined to form the features of the desired part. Injection molding is widely used for manufacturing a variety of parts, from the smallest component to entire body panels of cars.

Process characteristics

- Utilizes a ram or screw-type plunger to force molten plastic material into a mold cavity
- Produces a solid or open-ended shape that has conformed to the contour of the mold
- Uses thermoplastic or thermoset materials
- Produces a parting line, sprue, and gate marks
- Ejector pin marks are usually present

History

The first man-made plastic was invented in Britain in 1861 by Alexander Parkes. He publicly demonstrated it at the 1862 International Exhibition in London, calling the material he produced "Parkesine." Derived from cellulose, Parkesine could be heated, molded, and retain its shape when cooled. It was, however, expensive to produce, prone to cracking, and highly flammable.

In 1868, American inventor John Wesley Hyatt developed a plastic material he named Celluloid, improving on Parkes' invention so that it could be processed into finished form. Together with his brother Isaiah, Hyatt patented the first injection molding machine in 1872. This machine was relatively simple compared to machines in use today. It worked like a large hypodermic needle, using a plunger to inject plastic through a heated cylinder into a mold. The industry progressed slowly over the years, producing products such as collar stays, buttons, and hair combs.

The industry expanded rapidly in the 1940s because World War II created a huge demand for inexpensive, mass-produced products. In 1946, American inventor James Watson Hendry built the first screw injection machine, which allowed much more precise control over the speed of injection and the quality of articles produced. This machine also allowed material to be mixed before injection, so that colored or recycled plastic could be added to virgin material and mixed thoroughly before being injected. Today screw injection machines account for the vast majority of all injection machines. In the 1970s, Hendry went on to develop the first gas-assisted injection molding process, which permitted the production of complex, hollow articles that cooled quickly. This greatly improved design flexibility as well as the strength and finish of manufactured parts while reducing production time, cost, weight and waste.

The plastic injection molding industry has evolved over the years from producing combs and buttons to producing a vast array of products for many industries including automotive, medical, aerospace, consumer products, toys, plumbing, packaging, and construction.

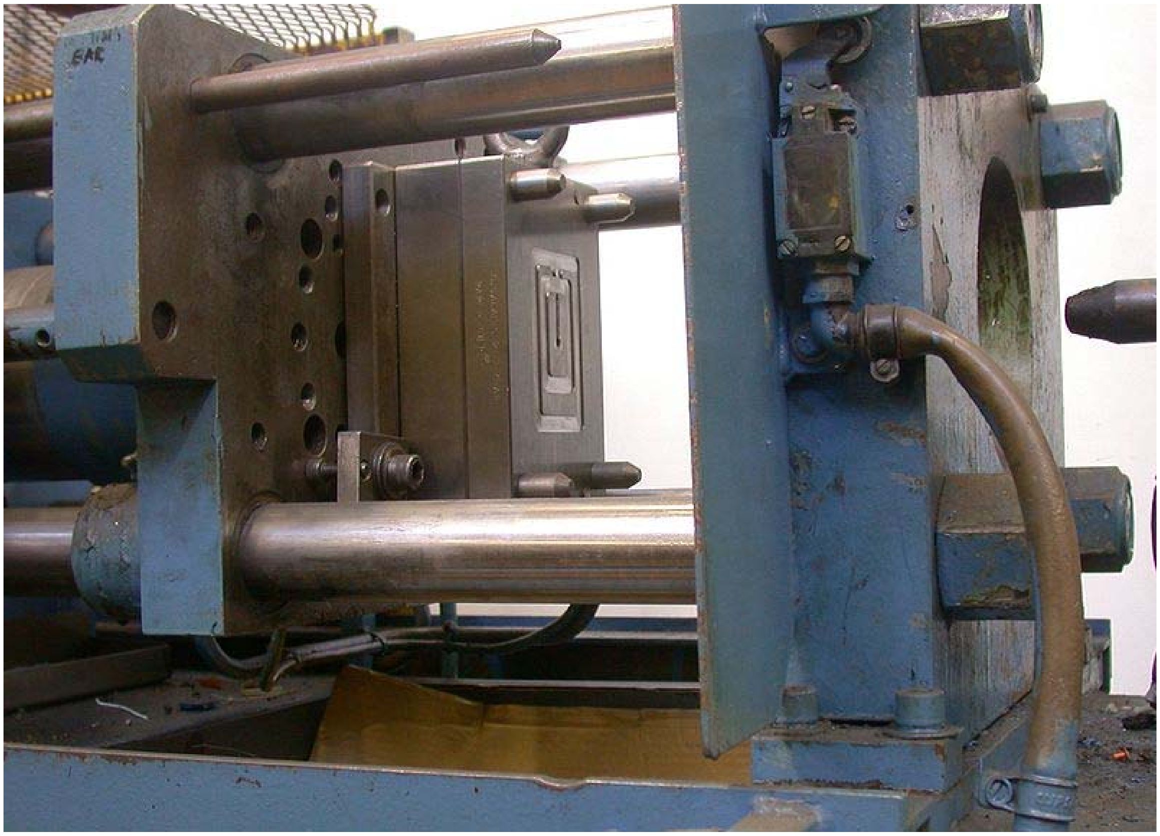
Applications

Injection molding is used to create many things such as wire spools, packaging, bottle caps, automotive dashboards, pocket combs, and most other plastic products available today. Injection molding is the most common method of part manufacturing. It is ideal for producing high volumes of the same object. Some advantages of injection molding are high production rates, repeatable high tolerances, the ability to use a wide range of materials, low labor cost, minimal scrap losses, and little need to finish parts after molding. Some disadvantages of this process are expensive equipment investment, potentially high running costs, and the need to design moldable parts.

Examples of polymers best suited for the process

Most polymers may be used, including all thermoplastics, some thermosets, and some elastomers. In 1995 there were approximately 18,000 different materials available for injection molding and that number was increasing at an average rate of 750 per year. The available materials are alloys or blends of previously developed materials meaning that product designers can choose from a vast selection of materials, one that has exactly the right properties. Materials are chosen based on the strength and function required for the final part, but also each material has different parameters for molding that must be taken into account. Common polymers like epoxy and phenolic are examples of thermosetting plastics while nylon, polyethylene, and polystyrene are thermoplastic.

Equipment



Paper clip mold opened in molding machine; the nozzle is visible at right

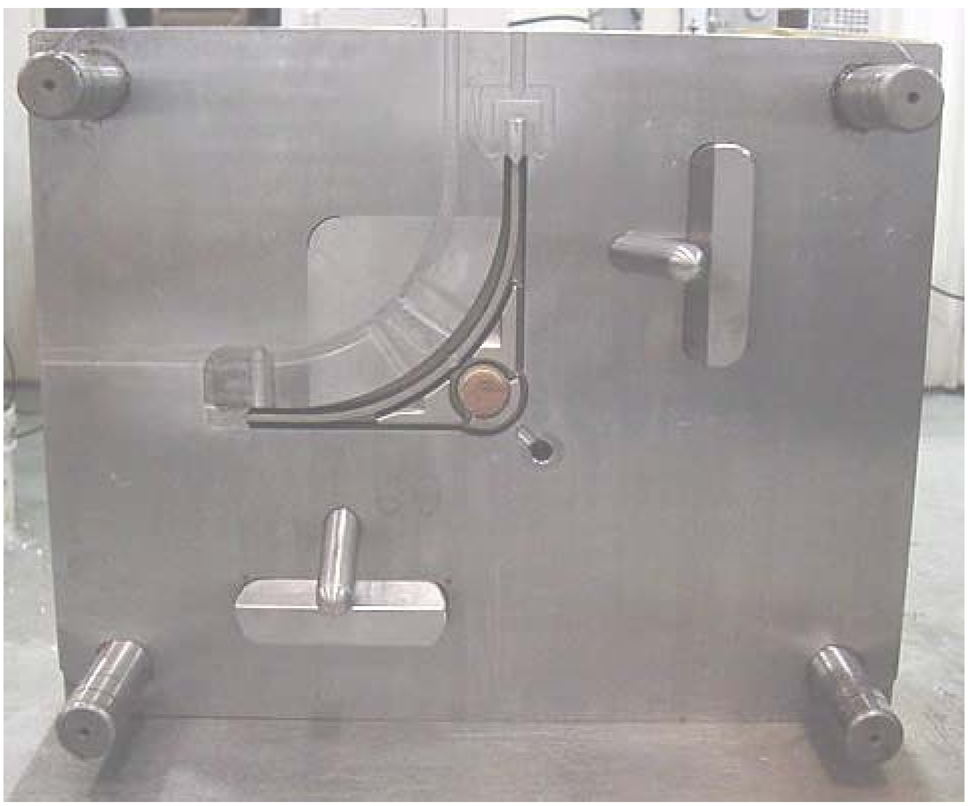
Injection molding machines consist of a material hopper, an injection ram or screw-type plunger, and a heating unit. They are also known as presses, they hold the molds in which the components are shaped. Presses are rated by tonnage, which expresses the amount of clamping force that the machine can exert. This force keeps the mold closed during the injection process. Tonnage can vary from less than 5 tons to 6000 tons, with the higher figures used in comparatively few manufacturing operations. The total clamp force needed is determined by the projected area of the part being molded. This projected area is multiplied by a clamp force of from 2 to 8 tons for each square inch of the projected areas. As a rule of thumb, 4 or 5 tons/in^2 can be used for most products. If the plastic material is very stiff, it will require more injection pressure to fill the mold, thus more clamp tonnage to hold the mold closed. The required force can also be determined by the material used and the size of the part, larger parts require higher clamping force.

Mold

Mold or **die** are the common terms used to describe the tooling used to produce plastic parts in molding.

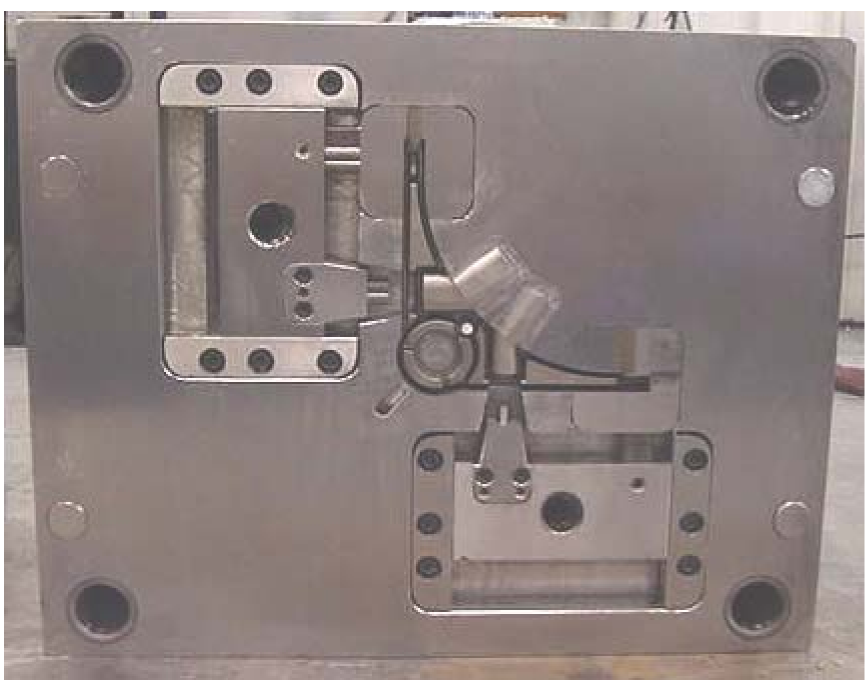
Since molds have been expensive to manufacture, they were usually only used in mass production where thousands of parts were being produced. Typical molds are constructed from hardened steel, pre-hardened steel, aluminum, and/or beryllium-copper alloy. The choice of material to build a mold from is primarily one of economics; in general, steel molds cost more to construct, but their longer lifespan will offset the higher initial cost over a higher number of parts made before wearing out. Pre-hardened steel molds are less wear-resistant and are used for lower volume requirements or larger components. The typical steel hardness is 38–45 on the Rockwell-C scale. Hardened steel molds are heat treated after machining. These are by far the superior in terms of wear resistance and lifespan. Typical hardness ranges between 50 and 60 Rockwell-C (HRC). Aluminum molds can cost substantially less, and, when designed and machined with modern computerized equipment, can be economical for molding tens or even hundreds of thousands of parts. Beryllium copper is used in areas of the mold that require fast heat removal or areas that see the most shear heat generated. The molds can be manufactured either by CNC machining or by using Electrical Discharge Machining processes

Injection molding die with side pulls



"A" side of die for 25% glass-filled acetal with 2 side pulls.

Close up of removable insert in "A" side.



"B" side of die with side pull actuators.

Insert removed from die.

Mold design

Standard two plates tooling – core and cavity are inserts in a mold base – "family mold" of five different parts

The mold consists of two primary components, the injection mold (A plate) and the ejector mold (B plate). Plastic resin enters the mold through a *sprue* in the injection mold, the sprue bushing is to seal tightly against the nozzle of the injection barrel of the molding machine and to allow molten plastic to flow from the barrel into the mold, also known as the *cavity*. The sprue bushing directs the molten plastic to the cavity images through channels that are machined into the faces of the A and B plates. These channels allow plastic to run along them, so they are referred to as runners. The molten plastic flows through the runner and enters one or more specialized gates and into the cavity geometry to form the desired part.

The amount of resin required to fill the sprue, runner and cavities of a mold is a shot. Trapped air in the mold can escape through air vents that are ground into the parting line of the mold. If the trapped air is not allowed to escape, it is compressed by the pressure of the incoming material and is squeezed into the corners of the cavity, where it prevents filling and causes other defects as well. The air can become so compressed that it ignites and burns the surrounding plastic material. To allow for removal of the molded part from the mold, the mold features must not overhang one another in the direction that the mold opens, unless parts of the mold are designed to move from between such overhangs when the mold opens (utilizing components called Lifters).

Sides of the part that appear parallel with the direction of draw (The axis of the cored position (hole) or insert is parallel to the up and down movement of the mold as it opens and closes) are typically angled slightly with (draft) to ease release of the part from the mold. Insufficient draft can cause deformation or damage. The draft required for mold release is primarily dependent on the depth of the cavity: the deeper the cavity, the more draft necessary. Shrinkage must also be taken into account when determining the draft required. If the skin is too thin, then the molded part will tend to shrink onto the cores that form them while cooling, and cling to those cores or part may warp, twist, blister or crack when the cavity is pulled away. The mold is usually designed so that the molded part reliably remains on the ejector (B) side of the mold when it opens, and draws the runner and the sprue out of the (A) side along with the parts. The part then falls freely when ejected from the (B) side. Tunnel gates, also known as submarine or mold gate, is located below the parting line or mold surface. The opening is machined into the surface of the mold on the parting line. The molded part is cut (by the mold) from the runner system on ejection from the mold. Ejector pins, also known as knockout pin, is a circular pin placed in either half of the mold (usually the ejector half), which pushes the finished molded product, or runner system out of a mold.

The standard method of cooling is passing a coolant (usually water) through a series of holes drilled through the mold plates and connected by hoses to form a continuous pathway. The coolant absorbs heat from the mold (which has absorbed heat from the hot plastic) and keeps the mold at a proper temperature to solidify the plastic at the most efficient rate.

To ease maintenance and venting, cavities and cores are divided into pieces, called *inserts*, and sub-assemblies, also called *inserts*, *blocks*, or *chase blocks*. By substituting interchangeable inserts, one mold may make several variations of the same part.

More complex parts are formed using more complex molds. These may have sections called slides, that move into a cavity perpendicular to the draw direction, to form overhanging part features. When the mold is opened, the slides are pulled away from the plastic part by using stationary “angle pins” on the stationary mold half. These pins enter a slot in the slides and cause the slides to move backward when the moving half of the mold opens. The part is then ejected and the mold closes. The closing action of the mold causes the slides to move forward along the angle pins.

Some molds allow previously molded parts to be reinserted to allow a new plastic layer to form around the first part. This is often referred to as overmolding. This system can allow for production of one-piece tires and wheels.

Two-shot or multi-shot molds are designed to "overmold" within a single molding cycle and must be processed on specialized injection molding machines with two or more injection units. This process is actually an injection molding process performed twice. In the first step, the base color material is molded into a basic shape. Then the second material is injection-molded into the remaining open spaces. That space is then filled during the second injection step with a material of a different color.

A mold can produce several copies of the same parts in a single "shot". The number of "impressions" in the mold of that part is often incorrectly referred to as cavitation. A tool with one impression will often be called a single impression(cavity) mold. A mold with 2 or more cavities of the same parts will likely be referred to as multiple impression (cavity) mold. Some extremely high production volume molds (like those for bottle caps) can have over 128 cavities.

In some cases multiple cavity tooling will mold a series of different parts in the same tool. Some toolmakers call these molds family molds as all the parts are related.

Effects on the material properties

The mechanical properties of a part are usually little affected. Some parts can have internal stresses in them. This is one of the reasons why it is desirable to have uniform wall thickness when molding. One of the physical property changes is shrinkage. A permanent chemical property change is the material thermoset, which can't be remelted to be injected again.

Tool materials

Tool steel or beryllium-copper are often used. Mild steel, aluminum, nickel or epoxy are suitable only for prototype or very short production runs. Modern hard aluminum (7075 and 2024 alloys) with proper mold design, can easily make molds capable of 100,000 or more part life.

Geometrical possibilities

The most commonly used plastic molding process, injection molding, is used to create a large variety of products with different shapes and sizes. Most importantly, they can create products with complex geometry that many other processes cannot. There are a few precautions when designing something that will be made using this process to reduce the risk of weak spots. First, streamline your product or keep the thickness relatively uniform. Second, try and keep your product between 2 to 20 inches.

The size of a part will depend on a number of factors (material, wall thickness, shape,process etc.). The initial raw material required may be measured in the form of granules, pellets or powders. Here are some ranges of the sizes:

Method	Raw materials	Maximum size	Minimum size
Injection molding (thermo-plastic)	Granules, pellets, powders	700 oz.	Less than 1 oz.
Injection molding (thermo-setting)	Granules, pellets, powders	200 oz.	Less than 1 oz.

Machining

Molds are built through two main methods: standard machining and EDM. Standard Machining, in its conventional form, has historically been the method of building injection molds. With technological development, CNC machining became the predominant means of making more complex molds with more accurate mold details in less time than traditional methods.

The electrical discharge machining (EDM) or spark erosion process has become widely used in mold making. As well as allowing the formation of shapes that are difficult to machine, the process allows pre-hardened molds to be shaped so that no heat treatment is required. Changes to a hardened mold by conventional drilling and milling normally require annealing to soften the mold, followed by heat treatment to harden it again. EDM is a simple process in which a shaped electrode, usually made of copper or graphite, is very slowly lowered onto the mold surface (over a period of many hours), which is immersed in paraffin oil. A voltage applied between tool and mold causes spark erosion of the mold surface in the inverse shape of the electrode.

Cost

The cost of manufacturing molds depends on a very large set of factors ranging from number of cavities, size of the parts (and therefore the mold), complexity of the pieces, expected tool longevity, surface finishes and many others. The initial cost is great, however the piece part cost is low, so with greater quantities the overall price decreases.

Injection process

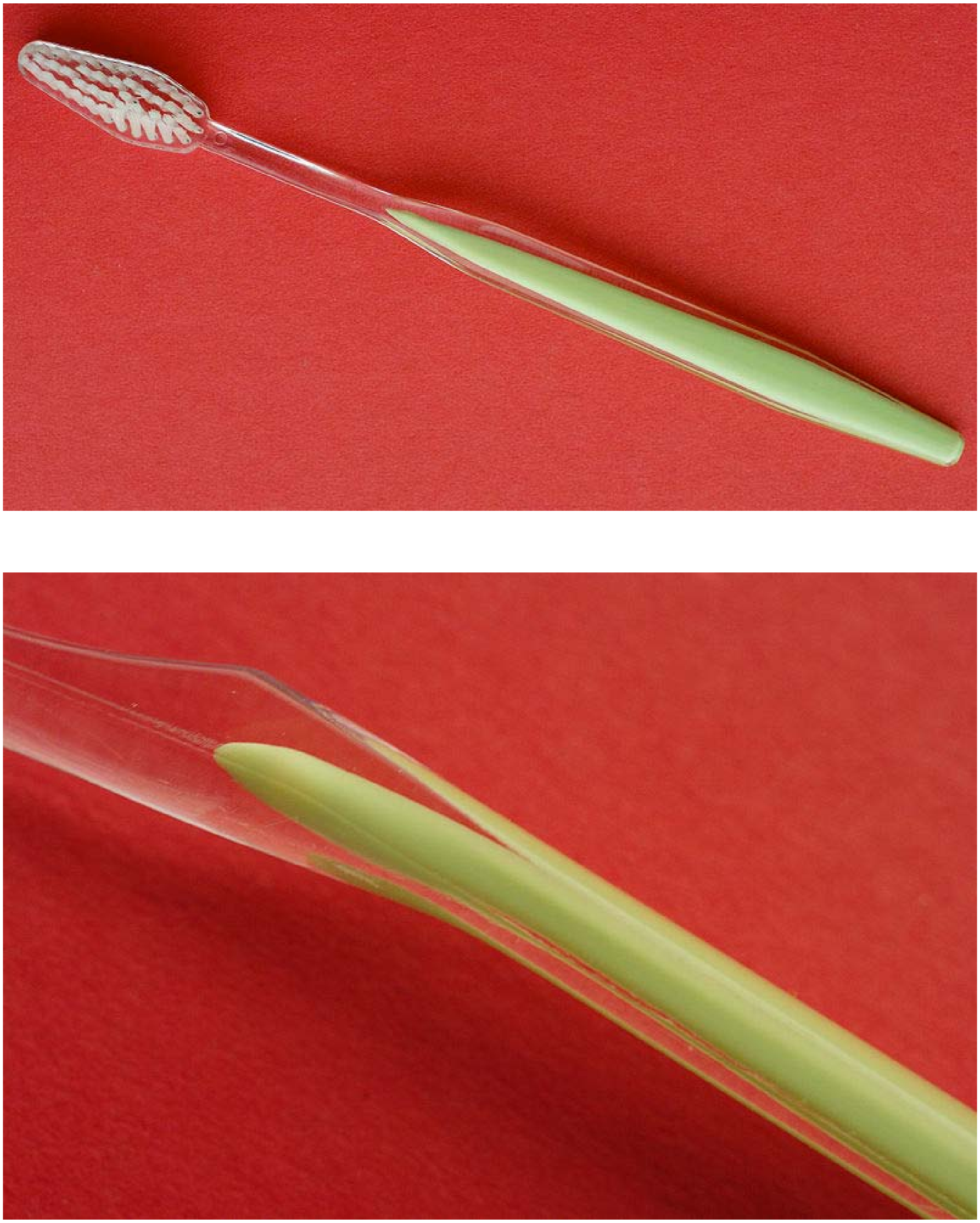
Small injection molder showing hopper, nozzle and die area

With injection molding, granular plastic is fed by gravity from a hopper into a heated barrel. As the granules are slowly moved forward by a screw-type plunger, the plastic is forced into a heated chamber, where it is melted. As the plunger advances, the melted plastic is forced through a nozzle that rests against the mold, allowing it to enter the mold cavity through a gate and runner system. The mold remains cold so the plastic solidifies almost as soon as the mold is filled.

Injection molding cycle

The sequence of events during the injection mold of a plastic part is called the injection molding cycle. The cycle begins when the mold closes, followed by the injection of the polymer into the mold cavity. Once the cavity is filled, a holding pressure is maintained to compensate for material shrinkage. In the next step, the screw turns, feeding the next shot to the front screw. This causes the screw to retract as the next shot is prepared. Once the part is sufficiently cool, the mold opens and the part is ejected.

Different types of injection molding processes



sandwich molded toothbrush handle

Although most injection molding processes are covered by the conventional process description above, there are several important molding variations including:

- Co-injection (sandwich) molding
- Fusible (lost, soluble) core injection molding
- Gas-assisted injection molding
- In-mold decoration and in mold lamination
- Injection-compression molding
- Insert and outsert molding
- Lamellar (microlayer) injection molding
- Low-pressure injection molding
- Metal injection molding
- Microinjection molding
- Microcellular molding
- Multicomponent injection molding
- Multiple live-feed injection molding
- Powder injection molding
- Push-Pull injection molding
- Reaction injection molding
- Resin transfer molding
- Rheomolding
- Structural foam injection molding
- Structural reaction injection molding
- Thin-wall molding
- Vibration gas injection molding
- Water assisted injection molding
- Rubber injection
- Injection_molding_of_liquid_silicone_rubber

Process troubleshooting

Optimal process settings are critical to influencing the cost, quality, and productivity of plastic injection molding. The main trouble in injection molding is to have a box of good plastics parts contaminated with scrap. For that reason process optimization studies have to be done and process monitoring has to take place. First article inspection of internal and external geometry including imperfections such as porosity can be completed using Industrial CT Scanning a 3D x-ray technology. For external geometry verification only a Coordinate-measuring machine or white light scanner can be used.

To have a constant filling rate in the cavity the switch over from injection phase to the holding phase can be made based on a cavity pressure level.
Having a stable production window the following issues are worth to investigate:
The **Metering phase** can be optimized by varying screw turns per minute and backpressure. Variation of time needed to reload the screw gives an indication of the stability of this phase.
Injection speed can be optimized by pressure drop studies between pressure measured in

the Nozzle (alternatively hydraulic pressure) and pressure measured in the cavity. Melted material with a lower viscosity has less pressure loss from nozzle to cavity than material with a higher viscosity. Varying the Injection speed changes the shear rate. Higher speed = higher shear rate = lower viscosity. Pay attention increasing the mold and melt temperature lowers the viscosity but lowers the shear rate too.

Gate seal or gate freeze / sink mark / weight and geometry studies have the approach to prevent sink marks and geometrical faults. Optimizing the high and duration of applied holding pressure based on cavity pressure curves is the appropriate way to go. The thicker the part the longer the holding pressure applied. The thinner the part the shorter the holding pressure applied.

Cooling time starts once the injection phase is finished. The hotter the melted plastics the longer the cooling time the thicker the part produced the longer the cooling time.

Molding trial

When filling a new or unfamiliar mold for the first time, where shot size for that mold is unknown, a technician/tool setter usually starts with a small shot weight and fills gradually until the mold is 95 to 99% full. Once this is achieved a small amount of holding pressure will be applied and holding time increased until gate freeze off (solidification time) has occurred. Gate freeze off time can be determined by increasing the hold time and then weighing the part when the weight of the part does not change we then know that the gate has frozen and no more material is injected into the part. Gate solidification time is important as it determines cycle time and the quality and consistency of the product, which itself is an important issue in the economics of the production process. Holding pressure is increased until the parts are free of sinks and part weight has been achieved. Once the parts are good enough and have passed any specific criteria, a setting sheet is produced for people to follow in the future. The method to setup an unknown mold the first time can be supported by installing cavity pressure sensors. Measuring the cavity pressure as a function of time can provide a good indication of the filling profile of the cavity. Once the equipment is set to successfully create the molded part, modern monitoring systems can save a reference curve of the cavity pressure. With that it is possible to reproduce the same part quality on another molding machine within a short setup time.

Molding defects

Injection molding is a complex technology with possible production problems. They can be caused either by defects in the molds or more often by part processing (molding)

Molding Defects	Alternative name	Descriptions	Causes
Blister	Blistering	Raised or layered zone on surface of the part	Tool or material is too hot, often caused by a lack of cooling around the tool or a faulty heater
Burn marks	Air burn/gas burn/dieseling	Black or brown burnt areas on the part located at	Tool lacks venting, injection speed is too high

		furthest points from gate or where air is trapped	
Color streaks (US)	Colour streaks (UK)	Localized change of color/colour	Masterbatch isn't mixing properly, or the material has run out and it's starting to come through as natural only. Previous colored material "dragging" in nozzle or check valve.
Delamination		Thin mica like layers formed in part wall	Contamination of the material e.g. PP mixed with ABS, very dangerous if the part is being used for a safety critical application as the material has very little strength when delaminated as the materials cannot bond
Flash	Burrs	Excess material in thin layer exceeding normal part geometry	Mold is over packed or parting line on the tool is damaged, too much injection speed/material injected, clamping force too low. Can also be caused by dirt and contaminants around tooling surfaces.
Embedded contaminates	Embedded particulates	Foreign particle (burnt material or other) embedded in the part	Particles on the tool surface, contaminated material or foreign debris in the barrel, or too much shear heat burning the material prior to injection
Flow marks	Flow lines	Directionally "off tone" wavy lines or patterns	Injection speeds too slow (the plastic has cooled down too much during injection, injection speeds must be set as fast as you can get away with at all times)
Jetting		Deformed part by turbulent flow of material	Poor tool design, gate position or runner. Injection speed set too high.
Knit lines	Weld lines	Small lines on the backside of core pins or windows in parts that look like just lines.	Caused by the melt-front flowing around an object standing proud in a plastic part as well as at the end of fill where the melt-front comes together again. Can be minimized or eliminated with a mold-flow study when the mold is in design phase. Once the mold is made and the gate is placed, one can minimize this flaw only by changing the melt and the mold temperature.
Polymer degradation		Polymer breakdown from hydrolysis, oxidation etc.	Excess water in the granules, excessive temperatures in barrel
Sink marks	[sinks]	Localized depression (In thicker zones)	Holding time/pressure too low, cooling time too short, with sprueless hot runners this can also be caused by the gate temperature being set too high. Excessive material or thick wall thickness.
Short shot	Non-fill / Short mold	Partial part	Lack of material, injection speed or pressure too low, mold too cold, lack of gas vents

Splay marks	Splash mark / Silver streaks	Circular pattern around gate caused by hot gas	Moisture in the material, usually when hygroscopic resins are dried improperly. Trapping of gas in "rib" areas due to excessive injection velocity in these areas. Material too hot.
Stringiness	Stringing	String like remain from previous shot transfer in new shot	Nozzle temperature too high. Gate hasn't frozen off
Voids		Empty space within part (Air pocket)	Lack of holding pressure (holding pressure is used to pack out the part during the holding time). Filling too fast, not allowing the edges of the part to set up. Also mold may be out of registration (when the two halves don't center properly and part walls are not the same thickness).
Weld line	Knit line / Meld line / Transfer line	Discolored line where two flow fronts meet	Mold/material temperatures set too low (the material is cold when they meet, so they don't bond). Point between injection and transfer (to packing and holding) too early.
Warping	Twisting	Distorted part	Cooling is too short, material is too hot, lack of cooling around the tool, incorrect water temperatures (the parts bow inwards towards the hot side of the tool) Uneven shrinking between areas of the part

Tolerances and surfaces

Molding tolerance is a specified allowance on the deviation in parameters such as dimensions, weights, shapes, or angles, etc. To maximize control in setting tolerances there is usually a minimum and maximum limit on thickness, based on the process used. Injection molding typically is capable of tolerances equivalent to an IT Grade of about 9–14. The possible tolerance of a thermoplastic or a thermoset is ±0.008 to ±0.002 inches. Surface finishes of two to four microinches or better can be obtained. Rough or pebbled surfaces are also possible.

Molding Type	Typical [in]	Possible [in]
Thermoplastic	±0.008	±0.002
Thermoset	±0.008	±0.002

Lubrication and cooling

Obviously, the mold must be cooled in order for the production to take place. Because of the heat capacity, inexpensiveness, and availability of water, water is used as the primary cooling agent. To cool the mold, water can be channeled through the mold to account for quick cooling times. Usually a colder mold is more efficient because this allows for faster cycle times. However, this is not *always* true because crystalline materials require the opposite: a warmer mold and lengthier cycle time.

Power requirements

The power required for this process of injection molding depends on many things and varies between materials used. *Manufacturing Processes Reference Guide* states that the power requirements depend on "a material's specific gravity, melting point, thermal conductivity, part size, and molding rate." Below is a table from page 243 of the same reference as previously mentioned that best illustrates the characteristics relevant to the power required for the most commonly used materials.

Material	Specific gravity	Melting point (°F)
Epoxy	1.12 to 1.24	248
Phenolic	1.34 to 1.95	248
Nylon	1.01 to 1.15	381 to 509
Polyethylene	0.91 to 0.965	230 to 243
Polystyrene	1.04 to 1.07	338

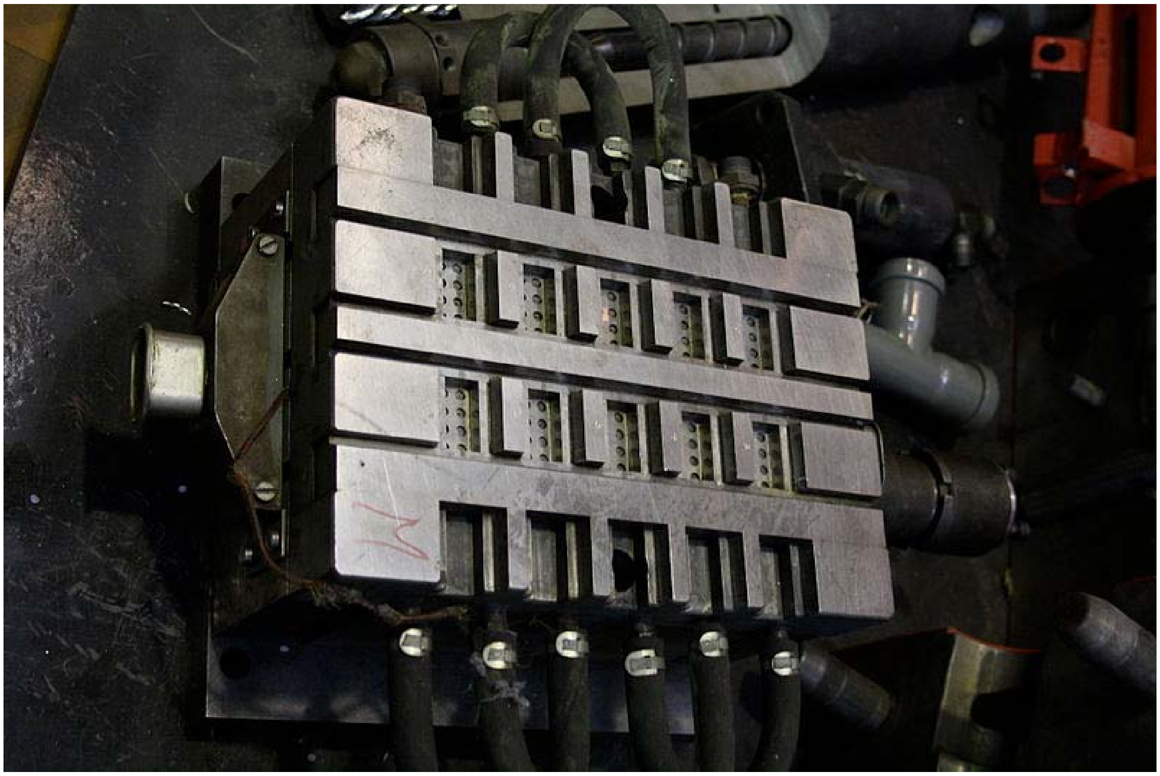
Inserts

Metal inserts can also be injection molded into the workpiece. For large volume parts the inserts are placed in the mold using automated machinery. An advantage of using automated components is that the smaller size of parts allows a mobile inspection system that can be used to examine multiple parts in a decreased amount of time. In addition to mounting inspection systems on automated components, multiple axial robots are also capable of removing parts from the mold and place them in latter systems that can be used to ensure quality of multiple parameters. The ability of automated components to decrease the cycle time of the processes allows for a greater output of quality parts.

Specific instances of this increased efficiency include the removal of parts from the mold immediately after the parts are created and use in conjunction with vision systems. The removal of parts is achieved by using robots to grip the part once it has become free from the mold after in ejector pins have been raised. The robot then moves these parts into either a holding location or directly onto an inspection system, depending on the type of product and the general layout of the rest of the manufacturer's production facility. Visions systems mounted on robots are also an advancement that has greatly changed the way that quality control is performed in insert molded parts. A mobile robot is able to more precisely determine the accuracy of the metal component and inspect more locations in the same amount of time as a human inspector.

Lego injection mold, lower side

Lego injection mold, detail of lower side

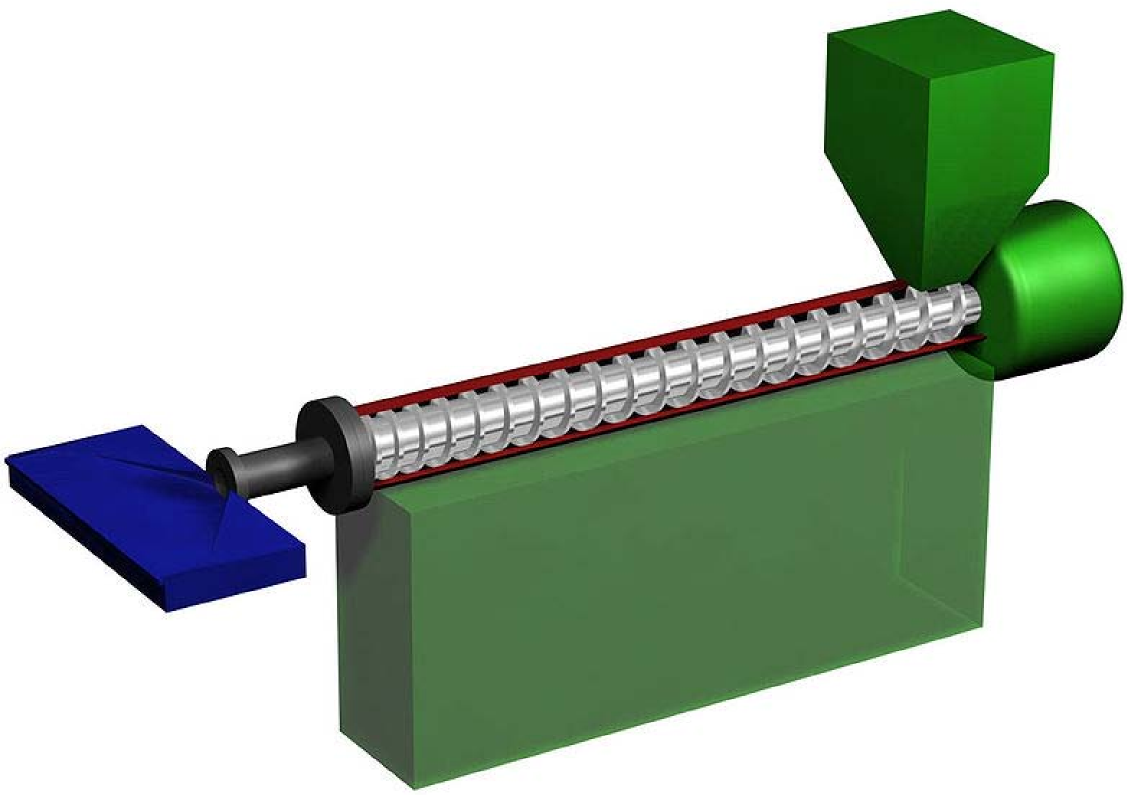


Lego injection mold, upper side

Lego injection mold, detail of upper side

Chapter 14

Plastics Extrusion



Cross-section of a plastic extruder to show the screw

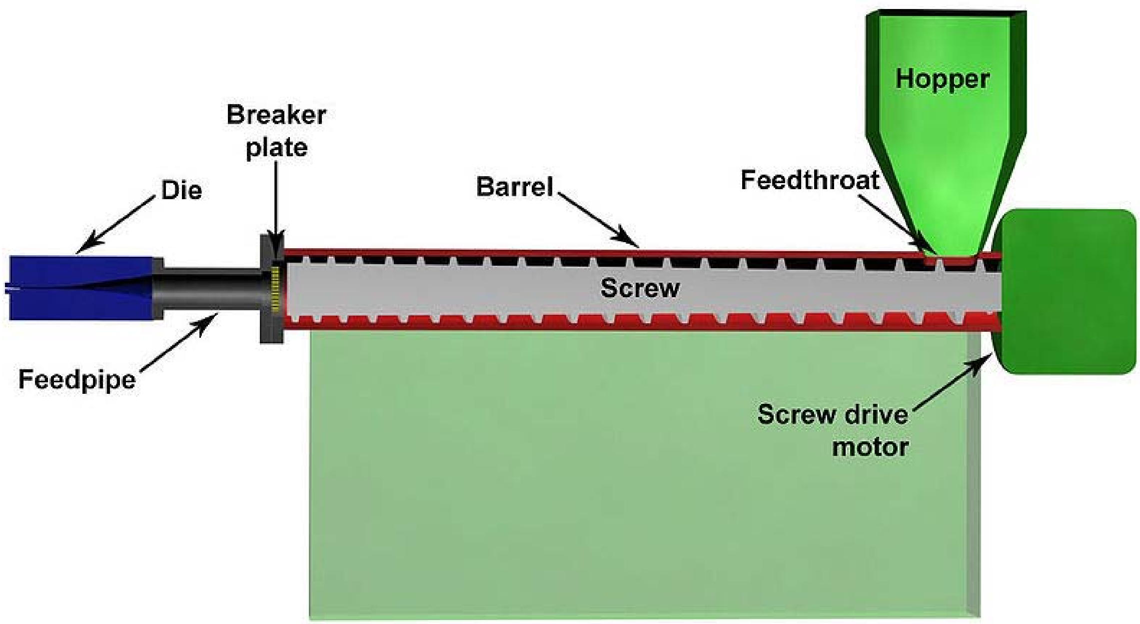
Plastics extrusion is a high volume manufacturing process in which raw plastic material is melted and formed into a continuous profile. Extrusion produces items such as pipe/tubing, weather stripping, fence, deck railing, window frames, adhesive tape and wire insulation.

Process

In the extrusion of plastics, raw thermoplastic material in the form of small beads (often called resin in the industry) is gravity fed from a top mounted hopper into the barrel of the extruder. Additives such as colorants and UV inhibitors (in either liquid or pellet form) are often used and can be mixed into the resin prior to arriving at the hopper.

The material enters through the feed throat (an opening near the rear of the barrel) and comes into contact with the screw. The rotating screw (normally turning at up to 120 rpm) forces the plastic beads forward into the barrel which is heated to the desired melt temperature of the molten plastic (which can range from 200 °C (392 °F) to 275 °C (527 °F) depending on the polymer). In most processes, a heating profile is set for the barrel in which three or more independent PID controlled heater zones gradually increase the temperature of the barrel from the rear (where the plastic enters) to the front. This allows the plastic beads to melt gradually as they are pushed through the barrel and lowers the risk of overheating which may cause degradation in the polymer.

Extra heat is contributed by the intense pressure and friction taking place inside the barrel. In fact, if an extrusion line is running a certain material fast enough, the heaters can be shut off and the melt temperature maintained by pressure and friction alone inside the barrel. In most extruders, cooling fans are present to keep the temperature below a set value if too much heat is generated. If forced air cooling proves insufficient then cast-in heater jackets are employed, and they generally use a closed loop of distilled water in heat exchange with tower or city water.



Plastic extruder cut in half to show the components

At the front of the barrel, the molten plastic leaves the screw and travels through a screen pack to remove any contaminants in the melt. The screens are reinforced by a breaker plate (a thick metal puck with many holes drilled through it) since the pressure at this point can exceed 5000 psi (34 MPa). The screen pack/breaker plate assembly also serves to create back pressure in the barrel. Back pressure is required for uniform melting and proper mixing of the polymer, and how much pressure is generated can be 'tweaked' by varying screen pack composition (the number of screens, their wire weave size, and other parameters). This breaker plate and screen pack combination also does the function of converting "rotational memory" of the molten plastic into "longitudinal memory".

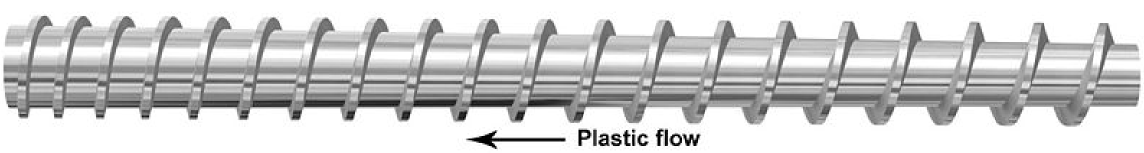
After passing through the breaker plate molten plastic enters the die. The die is what gives the final product its profile and must be designed so that the molten plastic evenly flows from a cylindrical profile, to the product's profile shape. Uneven flow at this stage would produce a product with unwanted stresses at certain points in the profile. These stresses can cause warping upon cooling. Almost any shape imaginable can be created so long as it is a continuous profile.

The product must now be cooled and this is usually achieved by pulling the extrudate through a water bath. Plastics are very good thermal insulators and are therefore difficult to cool quickly. Compared with steel, plastic conducts its heat away 2000 times more slowly. In a tube or pipe extrusion line, a sealed water bath is acted upon by a carefully controlled vacuum to keep the newly formed and still molten tube or pipe from collapsing. For products such as plastic sheeting, the cooling is achieved by pulling through a set of cooling rolls.

Sometimes on the same line a secondary process may occur before the product has finished its run. In the manufacture of adhesive tape, a second extruder melts adhesive and applies this to the plastic sheet while it's still hot. Once the product has cooled, it can be spooled, or cut into lengths for later use.

Screw design

There are five possible zones in a thermoplastic screw. Since terminology is not standardized in the industry, different names may refer to these zones. Different types of polymer will have differing screw designs, some not incorporating all of the possible zones.



A simple plastic extrusion screw

Most screws have these three zones:

- Feed zone. Also called solids conveying. This zone feeds the resin into the extruder, and the channel depth is usually the same throughout the zone.
- Melting zone. Also called the transition or compression zone. Most of the resin is melted in this section, and the channel depth gets progressively smaller.

- Metering zone. Also called melt conveying. This zone, in which channel depth is again the same throughout the zone, melts the last particles and mixes to a uniform temperature and composition.

In addition, a vented (two-stage) screw will have:

- Decompression zone. In this zone, about two-thirds down the screw, the channel suddenly gets deeper, which relieves the pressure and allows any trapped gases (usually moisture or air) to be drawn out by vacuum.
- Second metering zone. This zone is like the first metering zone, but with greater channel depth, and repressurizes the melt to get it through the resistance of the screens and the die.

Often screw length is referenced to its diameter as L:D ratio. For instance, a 6-inch (150 mm) diameter screw at 24:1 will be 144 inches (12 ft) long, and at 32:1 it is 192 inches (16 ft) long. An L:D ratio of 24:1 is common, but some machines go up to 32:1 for more mixing and more output at the same screw diameter. Two-stage (vented) screws are typically 36:1 to account for the two extra zones.

Each zone is equipped with one or more thermocouples or RTDs in the barrel wall for temperature control.

Geometrical possibilities

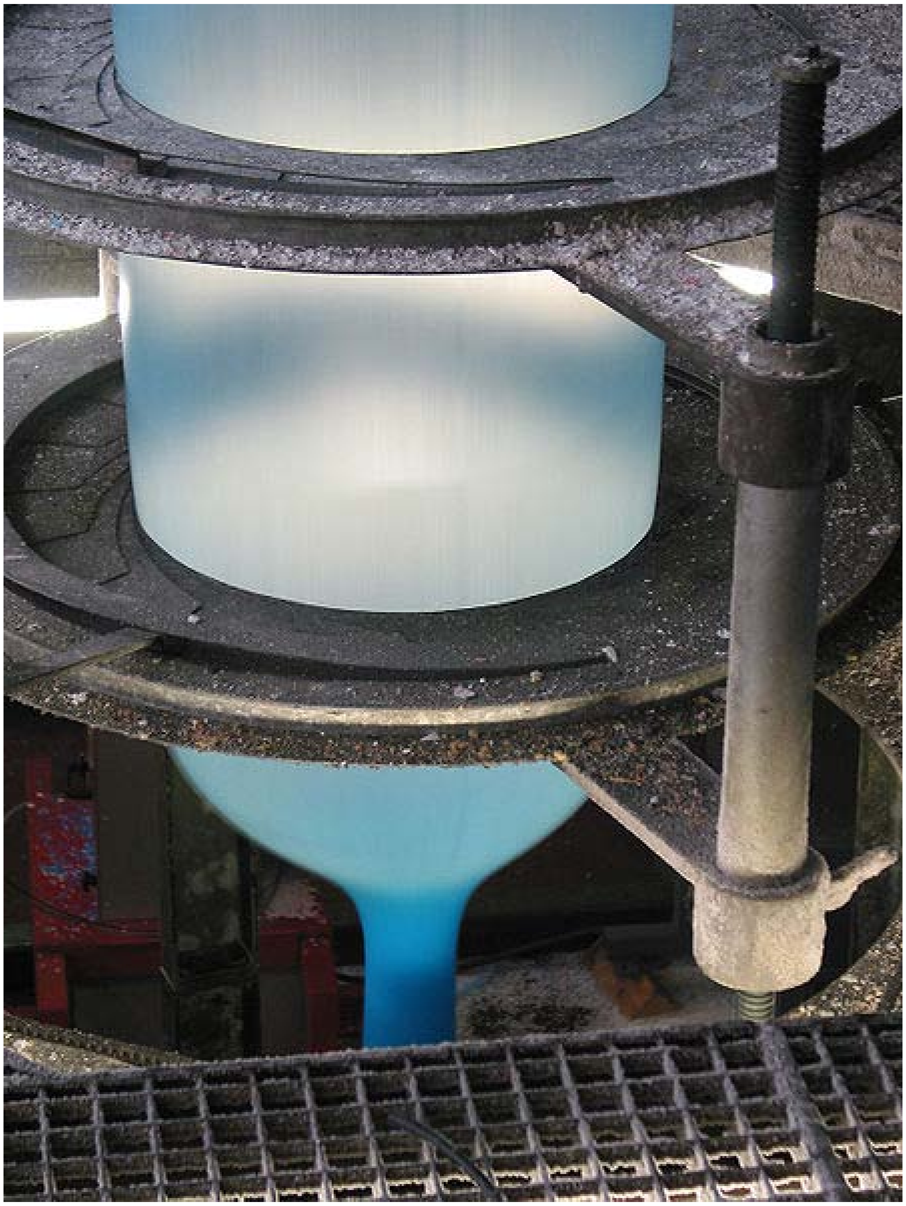
There are many geometrical possibilities when using extrusion. Thin film (flat or tubular) is the most common product. Other extruded products include pipe and tubing, coated paper or foil, monofilaments and textile fibers, flat sheet (anything over 0.010 inch (0.25 mm)), wire and cable covering, and a great variety of profiles such as window frames, gaskets and channels, and house siding. The products can be cut to length or rolled up as needed.

Typical extrusion materials

Typical plastic materials that are used in extrusion include but are not limited to: polyethylene, polypropylene, acetal, acrylic, nylon (polyamides), polystyrene, polyvinyl chloride, acrylonitrile butadiene styrene (ABS) and polycarbonate.

Types

Sheet/film extrusion



Blow extrusion of plastic film

For products such as plastic sheet or film, the cooling is achieved by pulling through a set of cooling rolls (calender or "chill" rolls), usually 3 or 4 in number. Running too fast creates an undesirable condition called "nerve"- basically, inadequate contact time is allowed to dissipate the heat present in the extruded plastic. In sheet extrusion, these rolls not only deliver the necessary cooling but also determine sheet thickness and surface texture (in case of structured rolls; i.e. smooth, levant, haircell, etc.).

Often co-extrusion is used to apply one or more layers on top of a base material to obtain specific properties such as UV-absorption, soft touch or "grip", matte surface, or energy reflection, where it is needed : on the surface.

A common post-extrusion process for plastic sheet stock is thermoforming, where the sheet is heated until soft (plastic), and formed via a mold into a new shape. When vacuum is used, this is often described as vacuum forming. Orientation (i.e. ability/ available density of the sheet to be drawn to the mold which can vary in depths from 1 to 36 inches typically) is highly important and greatly affects forming cycle times for most plastics.

Thermoforming can go from line bended pieces (e.g. displays) to complex shapes (computer housings), which often look like they have been injection moulded, thanks to the various possibilities in thermoforming, such as inserts, undercuts, divided moulds.

Plastic extrusion onto paper is the basis of the liquid packaging industry (juice cartons, wine boxes...); usually an aluminum layer is present as well. In food packaging plastic film is sometimes *metallised*.

Blown film extrusion

The manufacture of plastic film for products such as shopping bags is achieved using a blown film line.

This process is the same as a regular extrusion process up until the die. The die is an upright cylinder with a circular opening similar to a pipe die. The diameter can be a few centimetres to more than three metres across. The molten plastic is pulled upwards from the die by a pair of nip rolls high above the die (4 metres to 20 metres or more depending on the amount of cooling required). Changing the speed of these nip rollers will change the gauge (wall thickness) of the film. Around the die sits an air-ring. The air-ring cools the film as it travels upwards. In the centre of the die is an air outlet from which compressed air can be forced into the centre of the extruded circular profile, creating a bubble. This expands the extruded circular cross section by some ratio (a multiple of the die diameter). This ratio, called the “blow-up ratio” can be just a few percent to more than 200 percent of the original diameter. The nip rolls flatten the bubble into a double layer of film whose width (called the “layflat”) is equal to ½ the circumference of the bubble. This film can then be spooled or printed on, cut into shapes, and heat sealed into bags or other items.

An advantage of blown film extrusion over traditional film extrusion is that in the latter there are edges where there can be quality (thickness,..) variations.

Overjacketing extrusion

In a wire coating process, bare wire (or bundles of jacketed wires, filaments, etc.) is pulled through the center of a die similar to a tubing die. Many different materials are used for this purpose depending on the application. Essentially, an insulated wire is a thin walled tube which has been formed around a bare wire.

There are two different types of extrusion tooling used for coating over a wire. They are referred to as either "pressure" or "jacketing" tooling. The selection criteria for choosing which type of tooling to use is based on whether the particular application requires intimate contact or adhesion of the polymer to the wire or not. If intimate contact or adhesion is required, pressure tooling is used. If it is not desired, jacketing tooling is chosen.

The main difference in jacketing and pressure tooling is the position of the pin with respect to the die. For jacketing tooling, the pin will extend all the way flush with the die. When the bare wire is fed through the pin, it does not come in direct contact with the molten polymer until it leaves the die. For pressure tooling, the end of the pin is retracted inside the crosshead, where it comes in contact with the polymer at a much higher pressure.

Tubing extrusion

Extruded tubing process, such as drinking straws and medical tubing, is manufactured the same as a regular extrusion process up until the die. Hollow sections are usually extruded by placing a pin or mandrel inside of the die, and in most cases positive pressure is applied to the internal cavities through the pin.

Tubing with multiple lumens (holes) must be made for specialty applications. For these applications, the tooling is made by placing more than one pin in the center of the die, to produce the number of lumens necessary. In most cases, these pins are supplied with air pressure from different sources. In this way, the individual lumen sizes can be adjusted by adjusting the pressure to the individual pins.

Coextrusion

Coextrusion is the extrusion of multiple layers of material simultaneously. This type of extrusion utilizes two or more extruders to melt and deliver a steady volumetric throughput of different viscous plastics to a single extrusion head (die) which will extrude the materials in the desired form. This technology is used on any of the processes described above (blown film, overjacketing, tubing, sheet). The layer thicknesses are controlled by the relative speeds and sizes of the individual extruders delivering the materials.

There are a variety of reasons a manufacturer may choose coextrusion over single layer extrusion. One example is in the vinyl fencing industry, where coextrusion is used to tailor the layers based on whether they are exposed to the weather or not. Usually a thin layer of compound that contains expensive weather resistant additives are extruded on the outside while the inside has an additive package that is more suited for impact resistance and structural performance.

Extrusion coating

Extrusion coating is using a blown or cast film process to coat an additional layer onto an existing rollstock of paper, foil or film. For example, this process can be used to improve the characteristics of paper by coating it with polyethylene to make it more resistant to water. The extruded layer can also be used as an adhesive to bring two other materials together. A famous product that uses this technology is tetrapak.

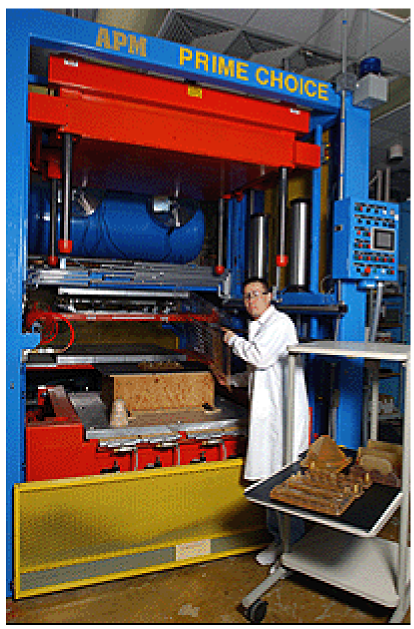
Compound extrusions

Compounding extrusion is a process that mixes one or more polymers with additives to give plastic compounds. The feeds may be pellets, powder and/or liquids, but the product is usually in pellet form, to be used in other plastic-forming processes such as extrusion and injection molding. Machine size varies from tiny lab machines to the biggest extruders in the industry, running as much as 20 tons per hour, as used by the chemical companies that make the base resins. Usually twin-screw extruders are preferred because they give better mixing at lower melt temperatures. Most of these have screws and barrels made up of smaller segments (mixing, conveying, venting and additive feeding) so that the design can be changed to meet the production and product needs. Single-screw extruders can be used for compounding as well, especially with appropriate screw design and static mixers after the screw. Selection of the components to be mixed (viscosities, additive carriers) is as important as the equipment.

Chapter 15

Thermoforming and Transfer Molding

Thermoforming



A vacuum/pressure assist thermoforming machine with molds visible in the lower right.

Thermoforming is a manufacturing process where a plastic sheet is heated to a pliable forming temperature, formed to a specific shape in a mold, and trimmed to create a usable product. The sheet, or "film" when referring to thinner gauges and certain material types, is heated in an oven to a high-enough temperature that it can be stretched into or onto a mold and cooled to a finished shape.

In its simplest form, a small tabletop or lab size machine can be used to heat small cut sections of plastic sheet and stretch it over a mold using vacuum. This method is often used for sample and protoype parts. In complex and high-volume applications, very large production machines are utilized to heat and form the plastic sheet and trim the formed parts from the sheet in a continuous high-speed process, and can produce many thousands of finished parts per hour depending on the machine and mold size and the size of the parts being formed.

Thermoforming differs from injection molding, blow molding, rotational molding, and other forms of processing plastics. Thin-gauge thermoforming is primarily the manufacture of disposable cups, containers, lids, trays, blisters, clamshells, and other products for the food, medical, and general retail industries. Thick-gauge thermoforming includes parts as diverse as vehicle door and dash panels, refrigerator liners, utility vehicle beds, and plastic pallets.

In the most common method of high-volume, continuous thermoforming of thin-gauge products, plastic sheet is fed from a roll or from an extruder into a set of indexing chains that incorporate pins, or spikes, that pierce the sheet and transport it through an oven for heating to forming temperature. The heated sheet then indexes into a form station where a mating mold and pressure-box close on the sheet, with vacuum then applied to remove trapped air and to pull the material into or onto the mold along with pressurized air to form the plastic to the detailed shape of the mold. (Plug-assists are typically used in addition to vacuum in the case of taller, deeper-draw formed parts in order to provide the needed material distribution and thicknesses in the finished parts.) After a short form cycle, a burst of reverse air pressure is actuated from the vacuum side of the mold as the form tooling opens, commonly referred to as air-eject, to break the vacuum and assist the formed parts off of, or out of, the mold. A stripper plate may also be utilized on the mold as it opens for ejection of more detailed parts or those with negative-draft, undercut areas. The sheet containing the formed parts then indexes into a trim station on the same machine, where a die cuts the parts from the remaining sheet web, or indexes into a separate trim press where the formed parts are trimmed. The sheet web remaining after the formed parts are trimmed is typically wound onto a take-up reel or fed into an inline granulator for recycling.

Most thermoforming companies recycle their scrap and waste plastic, either by compressing in a baling machine or by feeding into a granulator (grinder) and producing ground flake, for sale to reprocessing companies or re-use in their own facility. Frequently, scrap and waste plastic from the thermoforming process is converted back into extruded sheet for forming again.

Thin and thick gauge thermoforming

There are two general thermoforming process categories. Sheet thickness less than 1.5 mm (0.060 inches) is usually delivered to the thermoforming machine from rolls or from a sheet extruder. Thin-gauge roll-fed or inline extruded thermoforming applications are dominated by rigid or semi-rigid disposable packaging. Sheet thicknesses greater than 3 mm (0.120 inches) is usually delivered to the forming machine by hand or an auto-feed method already cut to final dimensions. Heavy, or thick-gauge, cut sheet thermoforming applications are primarily used as permanent structural components. There is a small but growing medium gauge market that forms sheet 1.5 mm to 3 mm in thickness.

Heavy-gauge forming utilizes the same basic process as continuous thin-gauge sheet forming, typically draping the heated plastic sheet over a mold. Many heavy-gauge forming applications use vacuum only in the form process, although some use two halves of mating form tooling and include air pressure to help form. Aircraft windscreens and machine gun turret windows spurred the advance of heavy-gauge forming technology during WWII. Heavy gauge parts are used as cosmetic surfaces on permanent structures such as automobiles, refrigerators, spas, and shower enclosures, and electrical and electronic equipment. Unlike most thin-gauge thermoformed parts, heavy-gauge parts are often hand-worked after forming for trimming to final shape or for additional drilling, cutting, or finishing, depending on the product. Heavy-gauge products typically are of a "permanent" end use nature, while thin-gauge parts are more often designed to be disposable or recyclable and are primarily used to package or contain a food item or product.

Engineering

Thermoforming has benefited from applications of engineering technology , although the basic forming process is very similar to what was invented many years ago. Microprocessor and computer controls on more modern machinery allow for greatly increased process control and repeatability of same-job setups from one production run to the next, usually with the ability to save oven heater and process timing settings between jobs. The ability to place formed sheet into an inline trim station for more precise trim registration has been hugely improved due to the common use of electric servo motors for chain indexing versus air cylinders, gear racks, and clutches on older machines. Electric servo motors are also used on some modern and more sophisticated forming machines for actuation of the machine platens where form and trim tooling are mounted, rather than air cylinders which have traditionally been the industry standard, giving more precise control over closing and opening speeds and timing of the tooling. Quartz and radiant-panel oven heaters generally provide more precise and thorough sheet heating over older cal-rod type heaters, and better allow for zoning of ovens into areas of adjustable heat.

An integral part of the thermoforming process is the tooling which is specific to each part that is to be produced. Thin gage thermoforming as described above is almost always performed on in-line machines and typically requires molds, plug assists, pressure boxes and all mounting plates as well as the trim tooling and stacker parts that pertain to the job. Thick or heavy gage thermoforming also requires tooling specific to each part, but because the part size can be very large, the molds can be cast aluminum or some other composite material as well as machined aluminum as in thin gage. Typically thick gauge parts must be trimmed on CNC routers or hand trimmed using saws or hand routers. Even the most sophisticated thermoforming machine is limited to the quality of the tooling. Some large thermoforming manufacturers choose to have design and tool making facilities in house while others will rely on outside tool-making shops to build the tooling.

Industry

The more than USD10 billion North American market has traditionally been ¾ thin gauge and ¼ heavy gauge. In 2003 there were about 150 thin gauge thermoformers in North America. Sixty percent formed proprietary products. Thirty percent were custom formers and 10 percent were OEMs with in-house forming capability. There were nearly a dozen thin-gauge formers having annual sales of at least USD100 million. The largest had annual sales in excess of USD1,000 million. There were about 250 heavy gauge formers in North America. Nearly all were custom formers. Only two or three heavy gauge formers had annual sales of more than USD100million. The largest had annual sales of about USD140 million.

Transfer molding

Transfer molding, like compression molding, is a process where the amount of molding material (usually a thermoset plastic) is measured and inserted before the molding takes place. The molding material is preheated and loaded into a chamber known as the *pot*. A plunger is then used to force the material from the pot through channels known as a sprue and runner system into the mold cavities. The mold remains closed as the material is inserted and is opened to release the part from the sprue and runner. The mold walls are heated to a temperature above the melting point of the mold material; this allows a faster flow of material through the cavities.

Transfer Molding. This is an automated operation that combines compression-, molding, and transfer-molding processes. This combination has the good surface finish, dimensional stability, and mechanical properties obtained in compression molding and the high-automation capability and low cost of injection molding and transfer molding. Transfer Molding is having a "piston and cylinder"-like device built into the mold so that the rubber is squirted into the cavity through small holes. A piece of uncured rubber is placed into a portion of the transfer mold called the "pot." The mold is closed and under hydraulic pressure the rubber or plastic is forced through a small hole (the "gate") into the cavity. The mold is held closed while the plastic or rubber cures. The plunger is raised up and the "transfer pad" material may be removed and thrown away. The transfer mold is opened and the part can be removed. The flash and the gate may need to be trimmed. Another key point is that a premeasured amount of thermosetting plastic in powder, preform, and even granular form can be placed into the heating chamber.

The molds in both compression and transfer molding remain closed until the curing reaction within the material is complete. Ejector pins are usually incorporated into the design of the molding tool and are used to push the part from the mold once it has hardened. These types of molding are ideal for high production runs as they have short production cycles. Transfer molding, unlike compression molding uses a closed mold, so smaller tolerances and more intricate parts can be achieved. The fixed cost of the tooling in transfer molding is greater than in compression molding and as both methods produce waste material, whether it be flash or the material remaining in the sprue and runners, transfer molding is the more expensive process.

Transfer molding (TM) (or resin transfer molding, RTM) differs from compression molding in that in TM the resin is inserted into the mold (or tool) which contains the layers of fibres or a preform, whereas in compression molding prepregs or molding compounds are in the mold which is then heated and pressure is applied. No further pressure is applied in TM.

In RTM the resin is injected or drawn into a mold, which contains the fibres, from a homogeniser under low pressure. The mold can be made from composites for low production cycles or with aluminium or steel for larger production. The differences between the two types being that metal has better heat transfer, hence quicker cycle times; metal lasts longer and deforms less, but at a higher cost. The main problem with this production route is that air can be trapped in mold and hence a method must be incorporated for allowing this air to escape. A number of solutions to the problem exist including extending one level of reinforcement beyond the cavity (with a 25% resin loss), appropriate vents and creating a vacuum in the mold (which also improves quality). Larger structures, better properties (less movement of fibres), increased flexibility of design and lower cost are some of the advantage this process has over compression molding due mainly to the low pressure injection. Other benefits include rapid manufacture, not labour intensive, ability to vary reinforcements easily or include cores such as foam and produce low and high quality products.

In the semiconductor industry, package encapsulation is usually done with transfer molding due to the high accuracy of transfer molding tooling and low cycle time of the process.

However, the drive to introduce "Green" manufacturing is becoming a mandatory process in most semicon assembly operations. New transfer mold designs integrated with suitable surface treatments like CrN, MiCC and H Cr plating are becoming more popular in the industry.

Some common products are utensil handles, electric appliance parts, electronic component, and connectors. Transfer molding is widely used to enclose or encapsulate items such as coils, integrated circuits, plugs, connectors, and other components.

Chapter 16

Fiberglass Molding and Pultrusion

Fiberglass molding

Fiberglass molding is a process in which fiberglass reinforced resin plastics are formed into useful shapes.

Mold Making

The fiberglass mold process begins with an object known as the plug or buck. This is an exact representation of the object to be made, and can be made from a variety of different materials. Certain types of foam are commonly used.

After the plug has been formed, it is sprayed with a mold release agent. The release agent will allow the mold to be separated from the plug once it is finished. The mold release agent is a special wax, and/or PVA (Polyvinyl alcohol). Polyvinyl Alcohol, however, is said to have negative effects on the final mold's surface finish.

Once the plug has its release agent applied, gelcoat is applied with a roller, brush or specially-designed spray gun. The gelcoat is pigmented resin, and gives the mold surface a harder, more durable finish.

Once the release agent and gelcoat are applied, layers of fiberglass and resin are laid-up onto the surface. The fiberglass used will typically be identical to that which will be used in the final product.

In the laying-up process, a layer of fiberglass mat is applied, and resin is applied over it. A special roller is then used to remove air bubbles. If left in the curing resin, air bubbles would significantly reduce the strength of the finished mold. The fiberglass spray lay-up process is also used to produce molds, and can provide good filling of corners and cavities where a glass mat or weave may prove to be too stiff.

Once the final layers of fiberglass are applied to the mould, the resin is allowed to set-up and cure. Wedges are then driven between the plug and the mold in order to separate the two.

Advanced techniques such as Resin Transfer Molding are also used.

Making a Component

The component-making process involves building up a component on the fiberglass mold. The mold is a *negative* image of the component to be made, so the fiberglass will be applied inside the mold, rather than around it.

As in the mold-making process, release agent is first applied to the mold. Colored gelcoat is then applied. Layers of fiberglass are then applied, using the same procedure as before. Once completed and cured, the component is separated from the mold using wedges, compressed air or both.

Pultrusion

Pultrusion is a continuous process of manufacturing of composite materials with constant cross-section whereby reinforced fibers are pulled through a resin, possibly followed by a separate preforming system, and into a heated die, where the resin undergoes polymerization. Many resin types may be used in pultrusion including polyester, polyurethane, vinylester and epoxy.

But the technology isn't limited to thermosetting resins. More recently, pultrusion has also been successfully used with thermoplastic matrices such as polybutylene terephthalate (PBT) either by powder impregnation of the glass fiber or by surrounding it with sheet material of the thermoplastic matrix which is then molten up.

Process

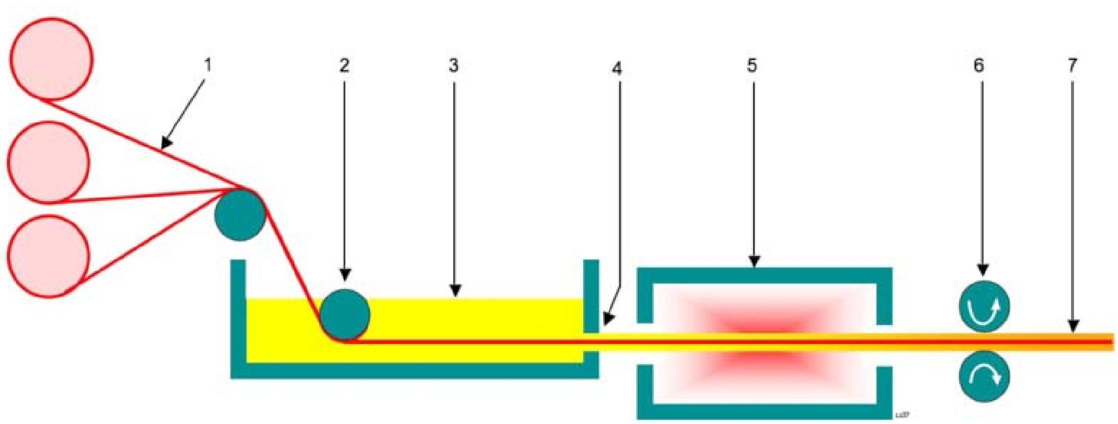


Diagram of the pultrusion process.

1 - Continuous roll of reinforced fibers/woven fiber mat
2 - Tension roller
3 - Resin bath
4 - Resin soaked fiber
5 - Die and heat source
6 - Pull mechanism
7 - Finished hardened fiber reinforced polymer

History

The term is a portmanteau word, combining "pull" and "extrusion".

The first pultrusion patent in the United States was issued in 1951. W. Brandt Goldsworthy is widely regarded as the inventor of pultrusion.

Equipment

The design of pultrusion machines varies. Two often used types are reciprocating (hand-over-hand) and continuous (cat-track).

Chapter 17

Filament Winding and Vacuum Forming

Filament winding

Filament winding is a fabrication technique for creating composite material structures. The process involves winding filaments under varying amounts of tension over a male mould or mandrel. The mandrel rotates while a carriage moves horizontally, laying down fibers in the desired pattern. The most common filaments are carbon or glass fiber and are coated with synthetic resin as they are wound. Once the mandrel is completely covered to the desired thickness, the mandrel is placed in an oven to solidify (set) the resin. Once the resin has cured, the mandrel is removed, leaving the hollow final product.

Filament winding is well suited to automation, where the tension on the filaments can be carefully controlled. Filaments that are applied with high tension results in a final product with higher rigidity and strength; lower tension results in more flexibility. The orientation of the filaments can also be carefully controlled so that successive layers are plied or oriented differently from the previous layer. The angle at which the fiber is laid down will determine the properties of the final product. A high angle "hoop" will provide crush strength, while a lower angle pattern (known as a closed or helical) will provide greater tensile strength.

Products currently being produced using this technique range from golf clubs, pipes, oars, bicycle forks, power and transmission poles, pressure vessels to missile casings, aircraft fuselages and lamp posts and yacht masts.

Fiberglass Laminating

Filament Winding can also be described as the manufacture of parts with high fiber volume fractions and controlled fiber orientation. Fiber tows are immersed in a resin bath where they are coated with low or medium molecular weight reactants. The impregnated tows are then literally wound around a mandrel (mold core) in a controlled pattern to form the shape of the part. After winding, the resin is then cured, typically using heat. The mold core may be removed or may be left as an integral component of the part(Rosato, D.V.).This process is primarily used for hollow, generally circular or oval sectioned components, such as pipes and tanks. Pressure vessels, pipes and drive shafts have all been manufactured using filament winding. It has been combined with other fiber application methods such as hand layup, pultrusion, and braiding. Compaction is through fiber tension and resin content is primarily metered. The fibers may be impregnated with resin before winding (wet winding), pre-impregnated (dry winding) or post-impregnated. Wet winding has the advantages of using the lowest cost materials with long storage life and low viscosity. The pre-impregnated systems produce parts with more consistent resin content and can often be wound faster.

Materials

Glass fibre is the fibre most frequently used for filament winding, carbon and aramid fibres are also used. Most high strength critical aerospace structures are produced with epoxy resins, with either epoxy or cheaper polyester resins being specified for most other applications. The ability to use continuous reinforcement without any breaks or joins is a definite advantage, as is the high fibre volume fraction that is obtainable, about 60% to 80%. Only the inner surface of a filament wound structure will be smooth unless a secondary operation is performed on the outer surface. The component is normally cured at high temperature before removing the mandrel. Finishing operations such as machining or grinding are not normally necessary.

Options

- Resins: Any, e.g. epoxy, polyester, vinylester, phenolic.
- Fibers: Glass, aramid, carbon and boron fibers. The fibers are used straight from a creel and not woven or stitched into a fabric form.
- Cores: Any, although components are usually single skin.

Process

- Uses a continuous length of fiber strand, roving, or tape
- Results in a shell of materials with a high strength-to-weight ratio
- Requires thermal curing of workpieces
- Patterns may be longitudinal, circumferential, or helical

Manufacturers

Examples of manufacturers that make large varieties of custom filament winding:

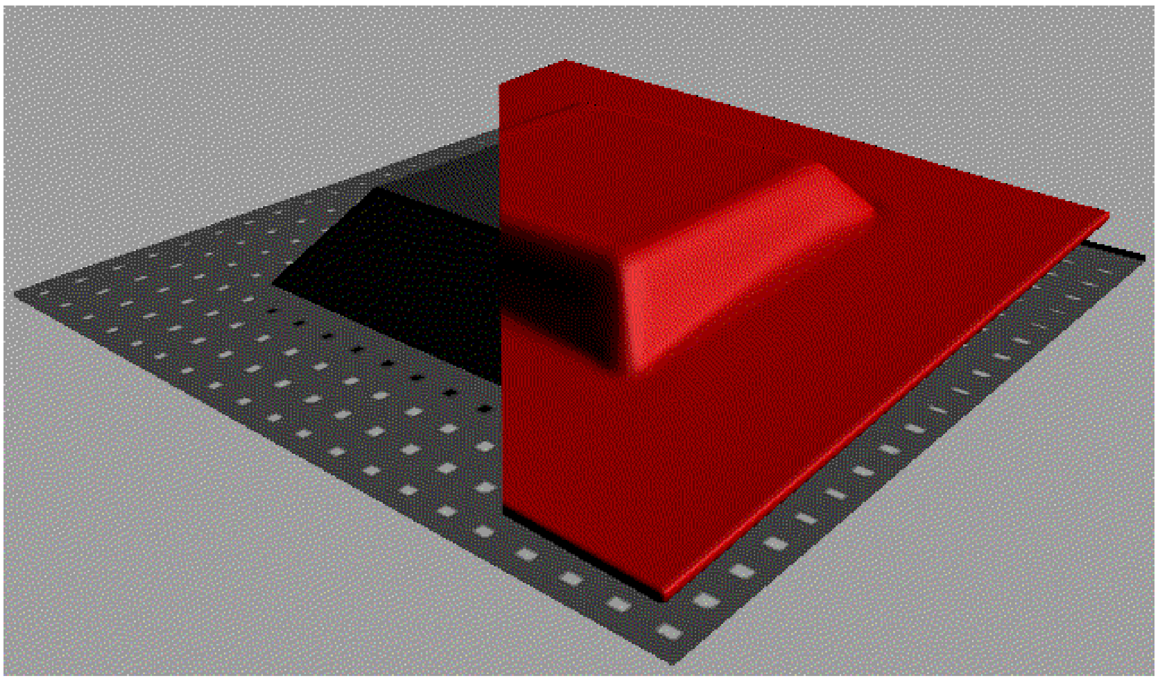
- Advanced Composites, Inc. (ACI)

- Future Pipe Industries (FPI)
- PCT
- PLP Comp
- Scorpius Space Launch Company (SSLC)

Examples of filament winding machine producers:

- Mikrosam A.D.

Vacuum forming



A simple visualization of the forming process

Vacuum forming, commonly known by people as **vacuuforming**, is a simplified version of thermoforming, whereby a sheet of plastic is heated to a forming temperature, stretched onto or into a single-surface mold (BrE, mould), and held against the mold by applying vacuum between the mold surface and the sheet. The vacuum forming process can be used to make most product packaging, speaker casings and even car dashboards.

Normally, draft angles must be present in the design on the mold (a recommended minimum of 3°), otherwise release of the formed plastic and the mold is very difficult.

Vacuum forming is usually – but not always – restricted to forming plastic parts that are rather shallow in depth. A thin sheet is formed into rigid cavities for unit doses of pharmaceuticals and for loose objects that are carded or presented as point-of-purchase items. Thick sheet is formed into permanent objects such as turnpike signs and protective covers.

Relatively deep parts can be formed if the form-able sheet is mechanically or pneumatically stretched prior to bringing it in contact with the mold surface and before vacuum is applied.

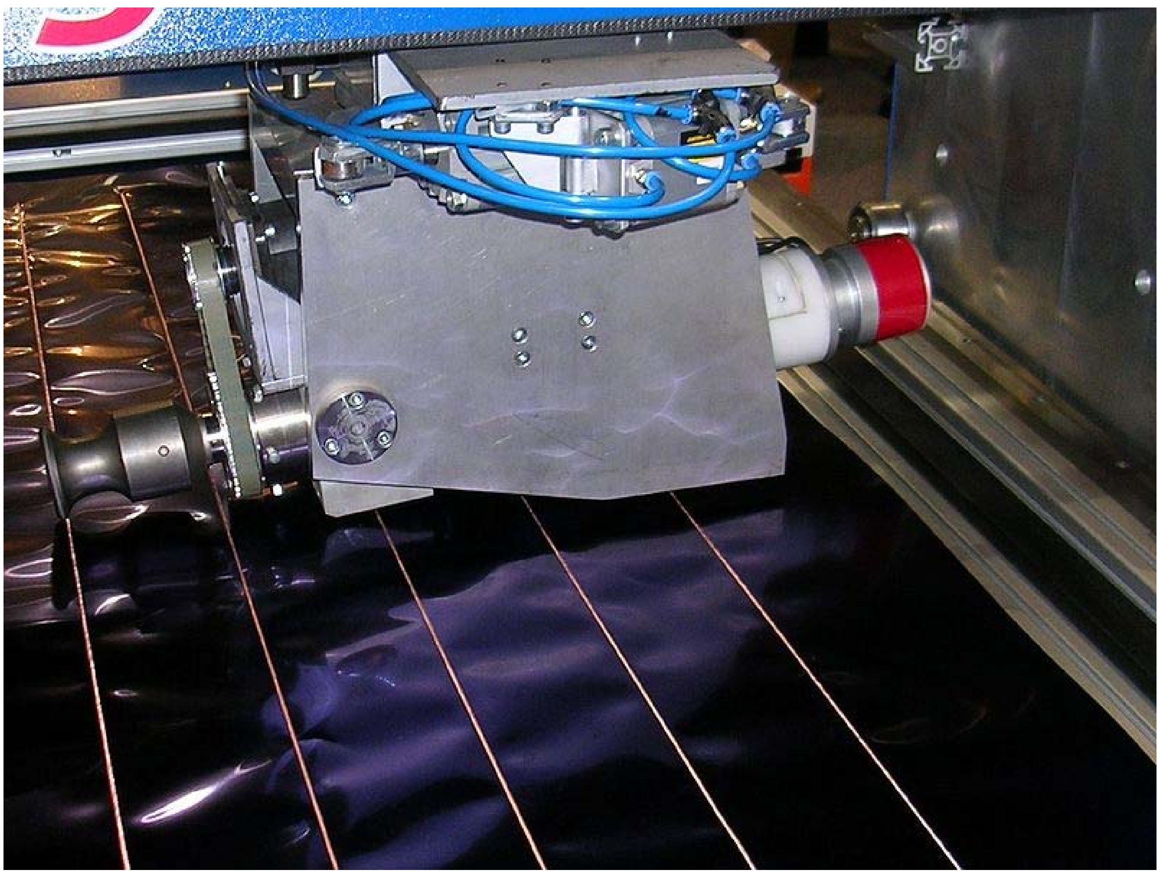
Suitable materials for use in vacuum forming are conventionally thermoplastics, the most common and easiest being High Impact Polystyrene Sheeting (HIPS). This is molded around a wood, structural foam or cast/machined aluminum mold and can form to almost any shape. Vacuum forming is also appropriate for transparent materials such as acrylic which are widely used in applications for aerospace such as passenger cabin window canopies for military fixed wing aircraft and "bubbles" for rotary wing aircraft.

Common problems encountered with vacuum forming

- Moisture absorption: absorbed moisture expands forming bubbles within the plastic's inner layers. This will be solved by drying the plastic for an extended period at high but sub-melting temperature.
- Webs form around the mold, which is due to overheating the plastic and so must be carefully monitored. Webbing can also occur when a mold is too large or parts of the mold are too close together.

Chapter 18

Ultrasonic Welding



Ultrasonic welding of thin metallic foils. The sonotrode is rotated along the weld seam.

Ultrasonic welding is an industrial technique whereby high-frequency ultrasonic acoustic vibrations are locally applied to workpieces being held together under pressure to create a solid-state weld. It is commonly used for plastics, and especially for joining dissimilar materials. In ultrasonic welding, there are no connective bolts, nails, soldering materials, or adhesives necessary to bind the materials together.

History

In 1960 Sonobond Ultrasonics, originally known as Aeroprojects, Incorporated, developed the first metal ultrasonic welding machine to be awarded a United States Patent.

Process

For joining complex injection molded thermoplastic parts, ultrasonic welding equipment can be easily customized to fit the exact specifications of the parts being welded. The parts are sandwiched between a fixed shaped nest (anvil) and a sonotrode (horn) connected to a transducer, and a ~20 kHz low-amplitude acoustic vibration is emitted. (Note: Common frequencies used in ultrasonic welding of thermoplastics are 15 kHz, 20 kHz, 30 kHz, 35 kHz, 40 kHz and 70 kHz). When welding plastics, the interface of the two parts is specially designed to concentrate the melting process. One of the materials usually has a spiked energy director which contacts the second plastic part. The ultrasonic energy melts the point contact between the parts, creating a joint. This process is a good automated alternative to glue, screws or snap-fit designs. It is typically used with small parts (e.g. cell phones, consumer electronics, disposable medical tools, toys, etc.) but it can be used on parts as large as a small automotive instrument cluster. Ultrasonics can also be used to weld metals, but are typically limited to small welds of thin, malleable metals, e.g. aluminum, copper, nickel. Ultrasonics would not be used in welding the chassis of an automobile or in welding pieces of a bicycle together, due to the power levels required.

Ultrasonic welding of thermoplastics causes local melting of the plastic due to absorption of vibration energy. The vibrations are introduced across the joint to be welded. In metals, Ultrasonic welding occurs due to high-pressure dispersion of surface oxides and local motion of the materials. Although there is heating, it is not enough to melt the base materials. Vibrations are introduced along the joint being welded.

Practical application of ultrasonic welding for rigid plastics was completed in the 1960s. At this point only hard plastics could be welded. The patent for the ultrasonic method for welding rigid thermoplastic parts was awarded to Robert Soloff and Seymour Linsley in 1965. Soloff, the founder of Sonics & Materials Inc., was a lab manager at Branson Instruments where thin plastic films were welded into bags and tubes using ultrasonic probes. He unintentionally moved the probe close to a plastic tape dispenser and the halves of the dispenser welded together. He realized that the probe did not need to be manually moved around the part but that the ultrasonic energy could travel through and around rigid plastics and weld an entire joint. He went on to develop the first ultrasonic press. The first application of this new technology was in the toy industry.

The first car made entirely out of plastic was assembled using ultrasonic welding in 1969. Even though plastic cars did not catch on ultrasonic welding did. The automotive industry has used it regularly since the 1980s. It is now used for a multitude of applications.

Ultrasonic welding can be used for both hard and soft plastics, such as semicrystalline plastics, and metals. Ultrasonic welding machines also have much more power now. The understanding of ultrasonic welding has increased with research and testing. The invention of more sophisticated and inexpensive equipment and increased demand for plastic and electronic components has led to a growing knowledge of the fundamental process. However, many aspects of ultrasonic welding still require more study, such as relating weld quality to process parameters. Ultrasonic welding continues to be a rapidly developing field.

Benefits of Ultrasonic welding are that it is much faster than conventional adhesives or solvents. Drying time is very quick, the pieces do not need to remain in a jig for long periods of time waiting for the joint to dry or cure. The welding can easily be automated also, making clean and precise joints. Site of the weld is also very clean not needing any touch up to material and bond.

Components

All ultrasonic welding systems are composed of the same basic elements:

- A press to put the 2 parts to be assembled under pressure
- A nest or anvil where the parts are placed and allowing the high frequency vibration to be directed to the interfaces
- An ultrasonic stack composed of a converter or piezoelectric transducer, an optional booster and a sonotrode (US: Horn). All three elements of the stack are specifically tuned to resonate at the same exact ultrasonic frequency (Typically 20, 30, 35 or 40 kHz)
    - Converter: Converts the electrical signal into a mechanical vibration
    - Booster: Modifies the amplitude of the vibration. It is also used in standard systems to clamp the stack in the press.
    - Sonotrode: Applies the mechanical vibration to the parts to be welded.
- An electronic ultrasonic generator (US: Power supply) delivering a high power AC signal with frequency matching the resonance frequency of the stack.
- A controller controlling the movement of the press and the delivery of the ultrasonic energy.

Applications

The applications of ultrasonic welding are extensive and are found in many industries including electrical and computer, automotive and aerospace, medical, and packaging. Whether two items can be ultrasonically welded is determined by their thickness. If they are too thick this process will not join them. This is the main obstacle in the welding of metals. However, wires, microcircuit connections, sheet metal, foils, ribbons and meshes are often joined using ultrasonic welding. Ultrasonic welding is a very popular technique for bonding thermoplastics. It is fast and easily automated with weld times often below one second and there is no ventilation system required to remove heat or exhaust. This type of welding is often used to build assemblies that are too small, too complex, or too delicate for more common welding techniques.

Computer and electrical industries

In the electrical and computer industry ultrasonic welding is often used to join wired connections and to create connections in small, delicate circuits. Junctions of wire harnesses are often joined using ultrasonic welding. Wire harnesses are large groupings of wires used to distribute electrical signals and power. Electric motors, field coils, transformers and capacitors may also be assembled with ultrasonic welding. It is also often preferred in the assembly of storage media such as flash drives and computer disks because of the high volumes required. Ultrasonic welding of computer disks has been found to have cycle times of less than 300 ms.

One of the areas in which ultrasonic welding is most used and where new research and experimentation is centered is microcircuits. This process is ideal for microcircuits since it creates reliable bonds without introducing impurities or thermal distortion into components. Semiconductor devices, transistors and diodes are often connected by thin aluminum and gold wires using ultrasonic welding. It is also used for bonding wiring and ribbons as well as entire chips to microcircuits. An example of where microcircuits are used is in medical sensors used to monitor the human heart in bypass patients.

One difference between ultrasonic welding and traditional welding is the ability of ultrasonic welding to join dissimilar materials. The assembly of battery components is a good example of where this ability is utilized. When creating battery and fuel cell components, thin gauge copper, nickel and aluminum connections, foil layers and metal meshes are often ultrasonically welded together. Multiple layers of foil or mesh can often be applied in a single weld eliminating steps and cost.

Aerospace and automotive industries

For automobiles, ultrasonic welding tends to be utilized in the assembly of large plastic components and electrical components such as instrument panels, door panels, lamps, air ducts, steering wheels, upholstery and engine components. As plastics have continued to replace other materials in the design and manufacture of automobiles, the assembly and joining of plastic components has increasingly become a critical issue. Some of the advantages for ultrasonic welding are low cycle times, automation, low capital costs, and flexibility. Also, ultrasonic welding does not damage surface finish, which is a crucial consideration for many car manufacturers, because the high-frequency vibrations prevent marks from being generated.

Ultrasonic welding is generally utilized in the aerospace industry when joining thin sheet gauge metals and other lightweight materials. Aluminum is a difficult metal to weld using traditional techniques because of its high thermal conductivity. However, it is one of the easier materials to weld using ultrasonic welding because it is a softer alloy metal and thus a solid-state weld is simple to achieve. Since aluminum is so widely used in the aerospace industry, it follows that ultrasonic welding is an important manufacturing process. Also, with the advent of new composite materials, ultrasonic welding is becoming even more prevalent. It has been used in the bonding of the popular composite material carbon fiber. Numerous studies have been done to find the optimum parameters that will produce quality welds for this material.

Medical industry

In the medical industry ultrasonic welding is often used because it does not introduce contaminants or degradation into the weld and the machines can be specialized for use in clean rooms. The process can also be highly automated, provides strict control over dimensional tolerances and does not interfere with the biocompatibility of parts. Therefore, it increases part quality and decreases production costs. Items such as arterial filters, anesthesia filters, blood filters, IV catheters, dialysis tubes, pipettes, cardiometry reservoirs, blood/gas filters, face masks and IV spike/filters can all be made using ultrasonic welding. Another important application in the medical industry for ultrasonic welding is textiles. Items like hospital gowns, sterile garments, masks, transdermal patches and textiles for clean rooms can be sealed and sewn using ultrasonic welding. This prevents contamination and dust production and reduces the risk of infection.

Packaging industry

Butane lighter

Packaging is perhaps the application in which ultrasonic welding is most often used. Many everyday items are either created or packaged using ultrasonic welding techniques. Sealing containers, tubes and blister packs are some common applications.

Ultrasonic welding is also applied in the packaging of dangerous materials such as explosives, fireworks and other reactive chemicals. These items tend to require hermetic sealing but cannot be subjected to high temperatures. One simple example of this application is the container for a butane lighter. This container weld must be able to withstand high pressure and stress and must be airtight to contain the butane. Another example is the packaging of ammunition and propellants. These packages must be able to withstand high pressure and stresses in order to protect the consumer from the contents. When sealing hazardous materials, safety is a primary concern.

The food industry finds ultrasonic welding preferable to traditional joining techniques because it is fast, sanitary and can produce hermetic seals. Milk and juice containers are examples of some products that are often sealed using ultrasonic welding. The paper parts to be sealed are coated with plastic, generally polypropylene or polyethylene, and then welded together to create an airtight seal. The main obstacle to overcome in this process is the setting of the parameters. For example, if over-welding occurs then the concentration of plastic in the weld zone may be too low and cause the seal to break. If it is under-welded the seal is incomplete. Variations in the thicknesses of materials can cause variations in weld quality. Some other food items that are sealed using ultrasonic welding include candy bar wrappers, frozen food packages and beverage containers.

The electrical and computer, automotive, aerospace, medical, and packaging industries are some of the industries which utilize ultrasonic welding. This process is used to assemble everything from microcircuits to milk cartons. It is increasing in popularity throughout many of these industries because of low cycle times, automation, low capital costs, flexibility, cleanliness, dimensional reliability and the bonding of dissimilar materials. Some of the drawbacks of ultrasonic welding are that its use is limited by the thickness of the materials, it may require expensive specialized tooling and it may generate noise.

Safety

Ultrasonic welding machines, like most industrial equipment, pose the risk of some hazards. These include exposure to high heat levels and voltages. This equipment should always be operated using the safety guidelines provided by the manufacturer in order to avoid injury. For instance, operators must never place hands or arms near the welding tip when the machine is activated. Also, operators should be provided with hearing protection and safety glasses. Operators should be informed of the OSHA regulations for the ultrasonic welding equipment and these regulations should be enforced.

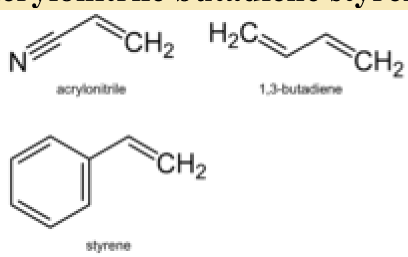
Ultrasonic welding machines must receive routine maintenance and inspection. Panel doors, housing covers and protective guards may need to be removed for maintenance. This should be done when the power to the equipment is off and only by the trained professional who is servicing the machine.

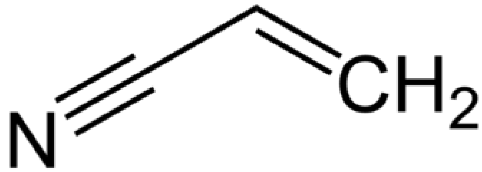
Since this is an ultrasonic process it would seem that sound would not be an issue. However, sub-harmonic vibrations, which can create annoying audible noise, may be caused in larger parts near the machine due to the ultrasonic welding frequency. This noise can be dampened by clamping these large parts at one or more locations. Also, high-powered welders with frequencies of 15 kHz and 20 kHz typically emit a potentially damaging high-pitched squeal in the range of human hearing. Shielding this radiating sound can be done using an acoustic enclosure. In short, there are hearing and safety concerns with ultrasonic welding that are important to consider, but generally they are comparable to those of other welding techniques.

Chapter 19

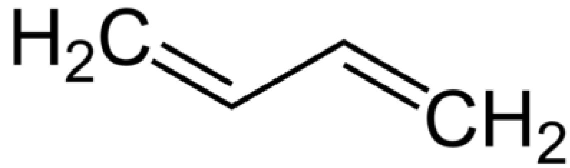
Acrylonitrile Butadiene Styrene and Polysulfone

Acrylonitrile butadiene styrene

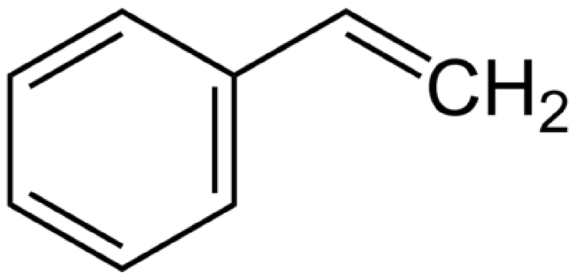
Acrylonitrile butadiene styrene	
	
Identifiers	
CAS number	9003-56-9 ✓
ChemSpider	23143 ✓
Properties	
Molecular formula	$(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$
Related compounds	
Related compounds	Acrylonitrile, butadiene and styrene (monomers)



acrylonitrile



1,3-butadiene



styrene

Monomers in ABS polymer

ABS polymer grains

Acrylonitrile butadiene styrene (**ABS**) (chemical formula $(C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$) is a common thermoplastic. Its melting point is approximately 105 °C (221 °F).

It is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-co-acrylonitrile). The nitrile groups from neighboring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The butadiene, a rubbery substance, provides resilience even at low temperatures. For the majority of applications, ABS can be used between −25 and 60 °C (-13 and 140 °F) as its mechanical properties vary with temperature. The properties are created by rubber toughening, where fine particles of elastomer are distributed throughout the rigid matrix.

Production of 1 kg of ABS requires the equivalent of about 2 kg of petroleum for raw materials and energy. It can also be recycled.

Properties

ABS is derived from acrylonitrile, butadiene, and styrene and carbon. Acrylonitrile is a synthetic monomer produced from propylene and ammonia; butadiene is a petroleum hydrocarbon obtained from the C4 fraction of steam cracking; styrene monomer is made by dehydrogenation of ethyl benzene — a hydrocarbon obtained in the reaction of ethylene and benzene.

The advantage of ABS is that this material combines the strength and rigidity of the acrylonitrile and styrene polymers with the toughness of the polybutadiene rubber.

The most important mechanical properties of ABS are impact resistance and toughness. A variety of modifications can be made to improve impact resistance, toughness, and heat resistance. The impact resistance can be amplified by increasing the proportions of polybutadiene in relation to styrene and also acrylonitrile, although this causes changes in other properties. Impact resistance does not fall off rapidly at lower temperatures. Stability under load is excellent with limited loads. Thus, changing the proportions of its components ABS can be prepared in different grades. Two major categories could be ABS for extrusion and ABS for injection moulding, then high and medium impact resistance. Generally ABS would have useful characteristics within a temperature range from 10 to 80 °C (50 to 176 °F).

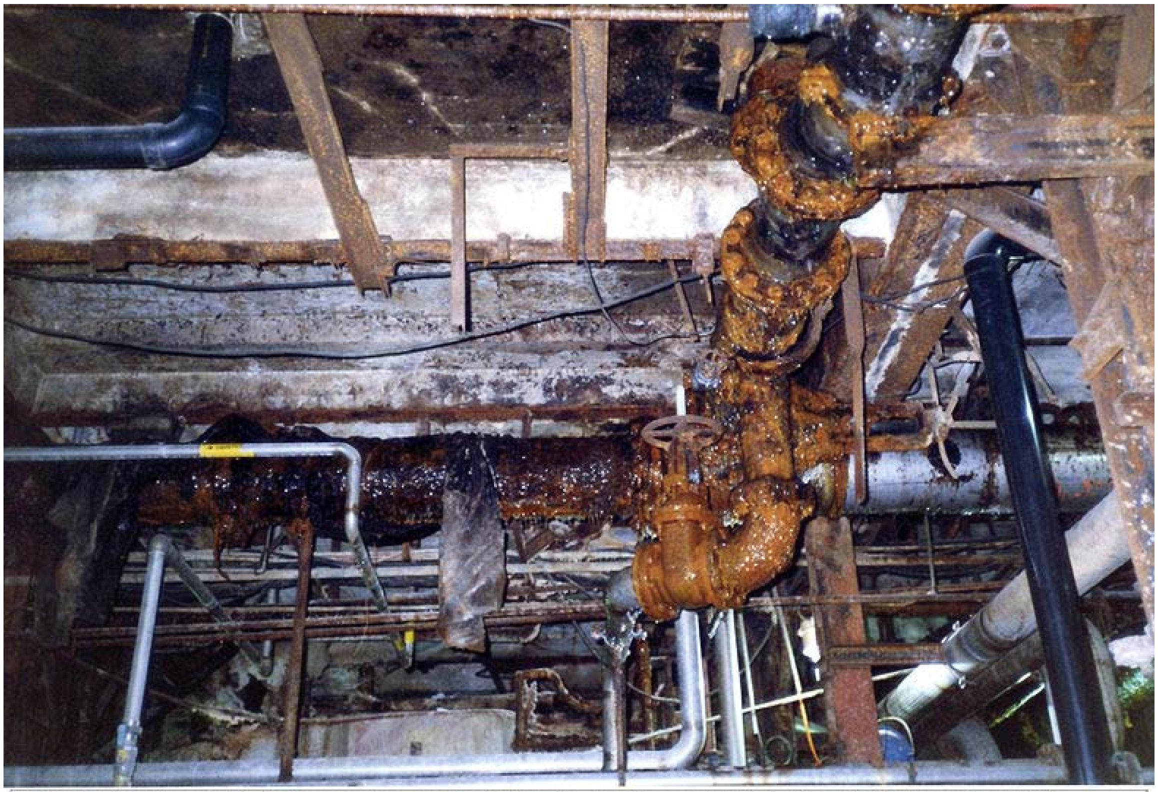
The final properties will be influenced to some extent by the conditions under which the material is processed to the final product. For example, molding at a high temperature improves the gloss and heat resistance of the product whereas the highest impact resistance and strength are obtained by molding at low temperature. Fibers (usually glass fibers) and additives can be mixed in the resin pellets to make the final product strong and raise the operating range to as high as 80 °C (176 °F). Pigments can also be added, as the raw material original color is translucent ivory to white. The aging characteristics of the polymers are largely influenced by the polybutadiene content, and it is normal to include antioxidants in the composition. Other factors include exposure to ultraviolet radiation, for which additives are also available to protect against.

Even though ABS plastics are used largely for mechanical purposes, they also have electrical properties that are fairly constant over a wide range of frequencies. These properties are little affected by temperature and atmospheric humidity in the acceptable operating range of temperatures.

ABS polymers are resistant to aqueous acids, alkalis, concentrated hydrochloric and phosphoric acids, alcohols and animal, vegetable and mineral oils, but they are swollen by glacial acetic acid, carbon tetrachloride and aromatic hydrocarbons and are attacked by concentrated sulfuric and nitric acids. They are soluble in esters, ketones, and ethylene dichloride.

While the cost of producing ABS is roughly twice the cost of producing polystyrene, ABS is considered superior for its hardness, gloss, toughness, and electrical insulation properties. It is degraded (dissolved) when exposed to acetone. ABS is flammable when it is exposed to high temperatures, such as a wood fire. It will melt, boil, then burst spectacularly into intense, hot flames.

Applications



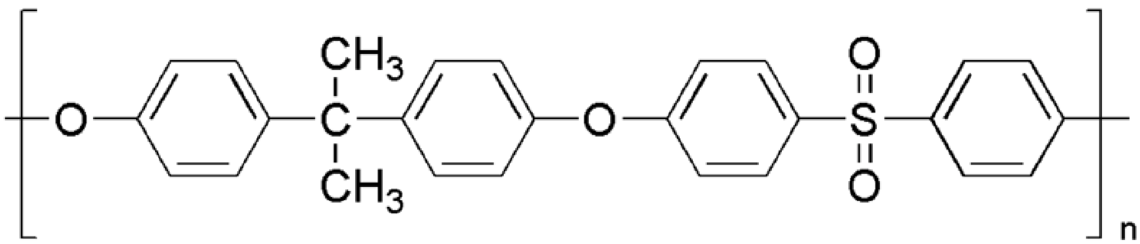
Pulp and paper mill, below a paper machine, in the basement. Lots of airborne humidity presents a housekeeping and corrosion prevention challenge. Sault Ste. Marie, Ontario, Canada, 1980's.

Black ABS plastic pipe (vertical, extreme right in photo) in use in a wet basement of a paper mill, in Sault Ste. Marie, Ontario.

The list of applications for ABS is long and continuously growing. Its light weight and ability to be injection molded and extruded make it useful in manufacturing products such as drain-waste-vent (DWV) pipe systems, musical instruments (recorders and plastic clarinets), golf club heads (due to its good shock absorbance), automotive trim components, automotive bumper bars, enclosures for electrical and electronic assemblies, protective headgear, whitewater canoes, buffer edging for furniture and joinery panels, luggage and protective carrying cases, small kitchen appliances, and toys, including Lego bricks.

ABS plastic ground down to an average diameter of less than 1 micrometer is used as the colorant in some tattoo inks. Tattoo inks that use ABS are extremely vivid. This vividness is the most obvious indicator that the ink contains ABS, as tattoo inks rarely list their ingredients.

Polysulfone



Polysulfone repeating unit.

Polysulfone describes a family of thermoplastic polymers. These polymers are known for their toughness and stability at high temperatures. They contain the subunit aryl-SO_2-aryl, the defining feature of which is the sulfone group. Polysulfones were introduced in 1965 by Union Carbide. Due to the high cost of raw materials and processing, polysulfones are used in specialty applications and often are a superior replacement for polycarbonates.

Production

A typical polysulfone is produced by the reaction of a diphenol and bis(4-chlorophenyl)sulfone, forming a polyether by elimination of sodium chloride:

$$n\ HOC_6H_4OH + n\ (ClC_6H_4)_2SO_2 + n\ Na_2CO_3 \rightarrow [OC_6H_4OC_6H_4SO_2C_6H_4]_n + 2n\ NaCl + n\ H_2O + n\ CO_2$$

The diphenol is typically bisphenol-A or, 1,4-dihydroxybenzene. Such step polymerizations require highly pure monomer to ensure high molecular weight products.

Chemical and physical properties

These polymers are rigid, high-strength, and transparent, retaining these properties between −100 °C and 150 °C. It has very high dimensional stability; the size change when exposed to boiling water or 150 °C air or steam generally falls below 0.1%. Its glass transition temperature is 185 °C.

Polysulfone is highly resistant to mineral acids, alkali, and electrolytes, in pH ranging from 2 to 13. It is resistant to oxidizing agents, therefore it can be cleaned by bleaches. It is also resistant to surfactants and hydrocarbon oils. It is not resistant to low-polar organic solvents (e.g. ketones and chlorinated hydrocarbons), and aromatic hydrocarbons. Mechanically, polysulfone has high compaction resistance, recommending its use under high pressures. It is also stable in aqueous acids and bases and many non-polar solvents; however it is soluble in dichloromethane and methylpyrrolidone.

Polyethersulfone (PES) is a similar polymer with low protein retention.

Applications

Polysulfone has the highest service temperature of all melt-processable thermoplastics. Its resistance to high temperatures gives it a role of a flame retardant, without compromising its strength that usually results from addition of flame retardants. Its high hydrolysis stability allows its use in medical applications requiring autoclave and steam sterilization. However, it has low resistance to some solvents and undergoes weathering; this weathering instability can be offset by adding other materials into the polymer.

Polysulfone allows easy manufacturing of membranes, with reproducible properties and controllable size of pores down to 40 nanometres. Such membranes can be used in applications like hemodialysis, waste water recovery, food and beverage processing, and gas separation. These polymers are also used in the automotive and electronic industries. Filter cartridges made from polysulfone membranes offer extremely high flow rates at very low differential pressures when compared with Nylon or polypropylene media. Additionally filter cartridges made from polysulfone can be sterilized with in line steam or in the autoclave with out loss of integrity up to 50 times.

Polysulfone can be reinforced with glass fibers. The resulting composite material has twice the tensile strength and three time increase of its modulus.

Polysulfone is used as a dielectric in capacitors.

It is supplied by Solvay Advanced Polymers, BASF, and PolyOne Corporation.

Polysulfone is also used as a copolymer.

Polysulfone is used as filtration media. The pore size can be very small, down to 0.2 µm or less for use in filter sterilization.

Polysulfone was the primary component of the gold-plated Lunar Extravehicular Visor Assembly, the iconic gold-film visor portion of the Apollo space-suits worn by Apollo astronauts during their lunar excursions.