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1. Introduction

1.1. Background
Many plastics are now used in such quantities that they have reached the status of commodity materials; indeed, the volume usage of plastics now comfortably exceeds that of metals. Much of the growth has taken place over the last thirty-five years, and the plastics industry is still expanding at twice the rate of the economy as a whole. The motivation for the rapid growth is the suitability of plastics for mass production, which depends mainly on their easy and reproducible shaping, and their low volume cost, coupled with some attractive properties. Shaping at low temperatures into complex forms is a characteristic of most plastics, and ensures their increasing use in spite of some shortcomings. The manufacturing industry has responded very positively to the increasing demand for plastics and for diversification of properties. The major feedstock is oil, the dependent petrochemicals industry supplies the monomers for plastics production, and manufactures a wide range of additives to modify their behavior(1).

1.2. Structure and properties of plastics

There are two subgroups of plastics: thermoplastics and cross-linked plastics. The former are linear chain polymers which soften on heating and solidify again on cooling, whereas the latter are network structures (in three dimensions) which once formed, are not softened by heating. The repetition of units in a polymer can result in a regularity of structure which may have important consequences, in favourable cases a number of chains may become aligned and in register for some distance, a state which is favoured on energy grounds, and which is termed crystallinity.

1.2.1. Mechanical properties

1.2.2. Thermal properties

1.2.3. Electrical properties

1.2.4. Optical properties

1.2.5. Melt properties

1.2.6. Chemical properties

1.3. Additives

Reference has already been made to antioxidants and UV stabilizers; these exemplify an important branch of plastics technology, the use of additives to modify the behaviour. Some additives are employed only in small concentration (0.1-1%) and are effective at this level, whereas others may constitute the major part of a plastics composition, being used, for example, to enhance the rigidity, or to reduce the cost. Additives used in low concentration include antioxidants, UV stabilizers, lubricants, slip and anti blocking additives for film surface modification, dyes an
pigments. Additives used mainly to improve mechanical properties or economics include particulate fillers, fibres and gases, the last resulting in foams. Dispersion of particles of a solid with modulus higher than that of the plastics matrix inevitably results in a composite of higher rigidity(2). The increase in rigidity is smallest for fillers of spherical shape, and greatest for those of high aspect ratio, particularly long fibres. For all fillers the effects are proportional to the volume fraction of the additive and, as well as mechanical properties, improvements in dimensional stability and reduced thermal expansion and contraction are observed. Conversely, some additives are used to reduce the stiffness, notably plasticizers and rubbers(2).

1.4. Processing of plastics

1.4.1. Thermoplastics processing

Melting
Mixing and homogenization
Melt transport
Primary shaping
Secondary shaping
Shape stabilization
Finishing operations.

1.4.2. Foams

1.4.3. Shaping of cross-linking plastics

1.5. Practical methods of processing

1.5.1. Thermoplastics processing

The techniques for primary shaping will be discussed first, to be followed by consideration of the more important techniques of secondary shaping

Extrusion is a continuous process which has the most economical output of all plastics shaping methods. Extruded products are simple in shape and have features in only two directions, being continuous in the third direction(3).

i. Injection moulding. Plastics material in granular or powder form is fed into the injection cylinder from the hopper, and is transported forward by rotation of the screw. Early injection presses used piston plungers to transport the melt, but from 1967 onwards, injection units have had reciprocating screw plungers.

Shot weight (PP) = shot weight (PS) x density of PP/density of PS

ii Calendering

iii Rotational moulding

iv Tubular film.

v Extrusion blow moulding. Most small and medium-sized enclosed containers, such as bottles and small drums, are produced by this process; more recently, complex shapes, including car fuel tanks and coolant reservoir tanks, have been blow moulded.

vi Injection blow moulding

vii Thermoforming
1.5.2. Processing methods for cross-linking plastics

i High-pressure moulding.
  - Compression moulding
  - Transfer moulding

ii Low-pressure moulding

iii Dual component dispensing techniques.

1.6. Interaction between shaping process and plastics materials

The stabilization stage, necessarily involving a phase change from liquid to solid, has several consequences (1).

i Shrinkage

ii Crystallinity

iii Crystalline texture

2. Cellulose-based plastics: celluloid and rayon

All Goodyear had done with vulcanization was improve the properties of a natural polymer. The next logical step was to use a natural polymer, cellulose, as the basis for a new material.

Inventors were particularly interested in developing synthetic substitutes for those natural materials that were expensive and in short supply, since that meant a profitable market to exploit. Ivory was a particularly attractive target for a synthetic replacement.

An Englishman from Birmingham named Alexander Parkes developed a "synthetic ivory" named "pyroxlin", which he marketed under the trade name "Parkesine", and which won a bronze medal at the 1862 World's fair in London. Parkesine was made from cellulose treated with nitric acid and a solvent. The output of the process hardened into a hard, ivory-like material that could be molded when heated.

However, Parkes was not able to scale up the process to an industrial level, and products made from Parkesine quickly warped and cracked after a short period of use. An American printer and amateur inventor named John Wesley Hyatt took up where Parkes left off. Parkes had failed for lack of a proper softener, but Hyatt discovered that camphor would do the job very nicely.

Hyatt was something of an industrial genius who understood what could be done with such a shapeable, or "plastic", material, and proceeded to design much of the basic industrial machinery needed to produce good-quality plastic materials in quantity. Since cellulose was the main constituent used in the synthesis of his new material, Hyatt named it "celluloid". It was introduced in 1863.

One of the first products were dental pieces, and sets of false teeth built around celluloid proved cheaper than existing rubber dentures. However, celluloid dentures tended to soften when hot, making tea drinking tricky, and the camphor taste tended to be difficult to suppress.
Celluloid's real breakthrough products were waterproof shirt collars, cuffs, and the false shirtfronts known as "dickies", whose unmanageable nature later became a stock joke in silent-movie comedies. They did not wilt and did not stain easily, and Hyatt sold them by trainloads. Corsets made with celluloid stays also proved popular, since perspiration did not rust the stays, as it would if they had been made of metal.

Celluloid proved extremely versatile in its field of application, providing a cheap and attractive replacement for ivory, tortoiseshell, and bone, and traditional products that had used these materials were much easier to fabricate with plastics. Some of the items made with celluloid in the nineteenth century were beautifully designed and implemented. For example, celluloid combs made to tie up the long tresses of hair fashionable at the time are now jewel-like museum pieces. Such pretty trinkets were no longer only for the rich.

Celluloid could also be used in entirely new applications. Hyatt figured out how to fabricate the material in a strip format for movie film. By the year 1900, movie film was a major market for celluloid.

However, celluloid still tended to yellow and crack over time, and it had another more dangerous defect: it burned very easily and spectacularly, unsurprising given that mixtures of nitric acid and cellulose are also used to synthesize smokeless powder.

Ping-pong balls, one of the few products still made with celluloid, sizzle and burn if set on fire, and Hyatt liked to tell stories about celluloid billiard balls exploding when struck very hard. These stories might have had a basis in fact, since the billiard balls were often celluloid covered with paints based on another, even more flammable, nitrocellulose product known as "collodion". If the balls had been imperfectly manufactured, the paints might have acted as primer to set the rest of the ball off with a bang.

Cellulose was also used to produce cloth. While the men who developed celluloid were interested in replacing ivory, those who developed the new fibers were interested in replacing another expensive material, silk.

In 1884, a French chemist, the Comte de Chardonnay, introduced a cellulose-based fabric that became known as "Chardonnay silk". It was an attractive cloth, but like celluloid it was very flammable, a property completely unacceptable in clothing. After some ghastly accidents, Chardonnay silk was taken off the market.

In 1894, three British inventors, Charles Cross, Edward Bevan, and Clayton Beadle, patented a new "artificial silk" or "art silk" that was much safer. The three men sold the rights for the new fabric to the French Courtauld company, a major manufacturer of silk, which put it into production in 1905, using cellulose from wood pulp as the "feedstock" material.

Art silk, technically known as Cellulose Acetate, became well known under the trade name "rayon", and was produced in great quantities through the 1930s, when it was supplanted by better artificial fabrics. It still remains in production today, often in blends with other natural and artificial fibers. It is cheap and feels smooth on the skin, though it is weak when wet and creases easily. It could also be produced in a transparent sheet form known as "cellophane". Cellulose Acetate became the
standard substrate for movie and camera film, instead of its very flammable predecessor.

3. Bakelite (phenolic)

The limitations of celluloid led to the next major advance, known as "phenolic" or "phenol-formaldehyde" plastics. A chemist named Leo Hendrik Baekeland, a Belgian-born American living in New York state, was searching for an insulating shellac to coat wires in electric motors and generators. Baekeland found that mixtures of phenol (C_6H_5OH) and formaldehyde (HCOH) formed a sticky mass when mixed together and heated, and the mass became extremely hard if allowed to cool and dry.

He continued his investigations and found that the material could be mixed with wood flour, asbestos, or slate dust to create "composite" materials with different properties. Most of these compositions were strong and fire resistant. The only problem was that the material tended to foam during synthesis, and the resulting product was of unacceptable quality.

Baekeland built pressure vessels to force out the bubbles and provide a smooth, uniform product. He publicly announced his discovery in 1909, naming it "bakelite". It was originally used for electrical and mechanical parts, finally coming into widespread use in consumer goods in the 1920s. When the Bakelite patent expired in 1927, the Catalin Corporation acquired the patent and began manufacturing Catalin plastic using a different process that allowed a wider range of coloring.

Bakelite was the first true plastic. It was a purely synthetic material, not based on any material or even molecule found in nature. It was also the first "thermoset" plastic. Conventional "thermoplastics" can be molded and then melted again, but thermoset plastics form bonds between polymers strands when "cured", creating a tangled matrix that cannot be undone without destroying the plastic. Thermoset plastics are tough and temperature resistant.

Bakelite was cheap, strong, and durable. It was molded into thousands of forms, such as radios, telephones, clocks, and, of course, billiard balls. The U.S. government even considered making one-cent coins out of it when World War II caused a copper shortage.

Phenolic plastics have been largely replaced by cheaper and less brittle plastics, but they are still used in applications requiring its insulating and heat-resistant properties. For example, some electronic circuit boards are made of sheets of paper or cloth impregnated with phenolic resin.

Phenolic sheets, rods and tubes are produced in a wide variety of grades under various brand names. The most common grades of industrial phenolic are Canvas, Linen and Paper.

4. Polystyrene and PVC
After the First World War, improvements in chemical technology led to an explosion in new forms of plastics. Among the earliest examples in the wave of new plastics were "polystyrene" (PS) and "polyvinyl chloride" (PVC), developed by IG Farben of Germany.

Polystyrene is a rigid, brittle, inexpensive plastic that has been used to make plastic model kits and similar knickknacks. It would also be the basis for one of the most popular "foamed" plastics, under the name "styrene foam" or "Styrofoam". Foam plastics can be synthesized in an "open cell" form, in which the foam bubbles are interconnected, as in an absorbent sponge, and "closed cell", in which all the bubbles are distinct, like tiny balloons, as in gas-filled foam insulation and floatation devices. In the late 1950s "High Impact" styrene was introduced, which was not brittle. It finds much current use as the substance of toy figurines and novelties.

PVC has side chains incorporating chlorine atoms, which form strong bonds. PVC in its normal form is stiff, strong, heat and weather resistant, and is now used for making plumbing, gutters, house siding, enclosures for computers and other electronics gear. PVC can also be softened with chemical processing, and in this form it is now used for shrink-wrap, food packaging, and raingear.

5. Nylon

The real star of the plastics industry in the 1930s was "polyamide" (PA), far better known by its trade name, "nylon". Nylon was the first purely synthetic fiber, introduced by Du Pont Corporation at the 1939 World's Fair in New York City.

In 1927, Du Pont had begun a secret development project designated "Fiber66", under the direction of Harvard chemist Wallace Carothers and chemistry department director Elmer Keiser Bolton. Carothers had been hired to perform pure research, and he worked to understand the new materials' molecular structure and physical properties. He took some of the first steps in the molecular design of the materials.

His work led to the discovery of synthetic nylon fiber, which was very strong but also very flexible. The first application was for bristles for toothbrushes. However, Du Pont's real target was silk, particularly silk stockings. Carothers and his team synthesized a number of different polyamides including polyamide6.6 and 4.6., they also discovered polyesters.
It took Du Pont twelve years and US$27 million to refine nylon synthesize and develop the industrial processes for bulk manufacture. With such a major investment, it was no surprise that Du Pont spared little expense to promote nylon after its introduction, creating a public sensation, or "nylon mania". Nylon mania came to an abrupt stop at the end of 1941 when the USA entered World War II. The production capacity that had been built up to produce nylon stockings, or just "nylons", for American women was taken over to manufacture vast numbers of parachutes for fliers and paratroopers. After the war ended, Du Pont went back to selling nylon to the public, engaging in another promotional campaign in 1946 that resulted in an even bigger craze, triggering the so called "nylon riots".

Subsequently polyamides 6, 10, 11, 12 have been developed based on monomers which are ring compounds, e.g. caprolactam.

Nylons still remains important plastics, and not just for use in fabrics. In its bulk form it is very wear resistant, particularly if oil-impregnated, and so is used to build gears, bearings, bushings, and because of good heat-resistance, increasing for under-the-hood applications in cars, and other mechanical parts.

### 6. Synthetic rubber

A polymer that was critical to the war effort was "synthetic rubber", which was produced in a variety of forms. Synthetic rubbers are not plastics. Synthetic rubbers are elastic materials.

The first synthetic rubber polymer was obtained by Lebedev in 1910. Practical synthetic rubber grew out of studies published in 1930 written independently by American Wallace Carothers, Russian scientist Lebedev and the German scientist Hermann Staudinger. These studies led in 1931 to one of the first successful synthetic rubbers, known as "neoprene", which was developed at DuPont under the direction of E.K. Bolton. Neoprene is highly resistant to heat and chemicals such as oil and gasoline, and is used in fuel hoses and as an insulating material in machinery.

In 1935, German chemists synthesized the first of a series of synthetic rubbers known as "Buna rubbers". These were "copolymers", meaning that their polymers were made up from not one but two monomers, in alternating sequence. One such Buna rubber, known as "GR-S" (Government Rubber Styrene), is a copolymer of butadiene and styrene, became the basis for U.S. synthetic rubber production during World War II.

Worldwide natural rubber supplies were limited and by mid-1942 most of the rubber-producing regions were under Japanese control. Military trucks needed rubber for tires, and rubber was used in almost every other war machine. The U.S. government
launched a major (and largely secret) effort to develop and refine synthetic rubber. A principal scientist involved with the effort was Edward Robbins.

By 1944 a total of 50 factories were manufacturing it, pouring out a volume of the material twice that of the world's natural rubber production before the beginning of the war.

After the war, natural rubber plantations no longer had a stranglehold on rubber supplies, particularly after chemists learned to synthesize isoprene. GR-S remains the primary synthetic rubber for the manufacture of tires.

Synthetic rubber would also play an important part in the space race and nuclear arms race. Solid rockets used during World War II used nitrocellulose explosives for propellants, but it was impractical and dangerous to make such rockets very big.

During the war, California Institute of Technology (Caltech) researchers came up with a new solid fuel, based on asphalt fuel mixed with an oxidizer, such as potassium or ammonium perchlorate, plus aluminium powder, which burns very hot. This new solid fuel burned more slowly and evenly than nitrocellulose explosives, and was much less dangerous to store and use, though it tended to flow slowly out of the rocket in storage and the rockets using it had to be stockpiled nose down.

After the war, the Caltech researchers began to investigate the use of synthetic rubbers instead of asphalt as the fuel in the mixture. By the mid-1950s, large missiles were being built using solid fuels based on synthetic rubber, mixed with ammonium perchlorate and high proportions of aluminium powder. Such solid fuels could be cast into large, uniform blocks that had no cracks or other defects that would cause nonuniform burning. Ultimately, all large military rockets and missiles would use synthetic rubber based solid fuels, and they would also play a significant part in the civilian space effort.

7. Plastics explosion: acrylic, polyethylene, etc.

Other plastics emerged in the prewar period, though some would not come into widespread use until after the war.

By 1936, American, British, and German companies were producing polymethyl methacrylate (PMMA), better known as "acrylic". Although acrylics are now well known for their use in paints and synthetic fibers, such as "fake furs", in their bulk form they are actually very hard and more transparent than glass, and are sold as glass replacements under trade names such as "Plexiglas" and "Lucite". Plexiglas was used to build aircraft canopies during the war, and it is also now used as a marble replacement for countertops.

Another important plastic, "polyethylene" (PE), sometimes known as "polythene", was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant Imperial Chemical Industries (ICI). This material evolved into two forms, "low density polyethylene" (LDPE), and "high density polyethylene" (HDPE).
PEs are cheap, flexible, durable, and chemically resistant. LDPE is used to make films and packaging materials, while HDPE is used for containers, plumbing, and automotive fittings. While PE has low resistance to chemical attack, it was found later that a PE container could be made much more robust by exposing it to fluorine gas, which modified the surface layer of the container into the much tougher "polyfluoroethylene".

Polyethylene would lead after the war to an improved material, "polypropylene" (PP), which was discovered in the early 1950s by Giulio Natta. It is common in modern science and technology that the growth of the general body of knowledge can lead to the same inventions in different places at about the same time, but polypropylene was an extreme case of this phenomenon, being separately invented about nine times. The ensuing litigation was not resolved until 1989.

Polypropylene managed to survive the legal process, and two American chemists working for Phillips Petroleum, J. Paul Hogan and Robert Banks, are now generally credited as the "official" inventors of the material. Polypropylene is similar to its ancestor, polyethylene, and shares polyethylene's low cost, but it is much more robust. It is used in everything from plastic bottles to carpets to plastic furniture, and is very heavily used in automobiles.

Polyurethane was invented by Friedrich Bayer & Company in 1937, and would come into use after the war, in blown form for mattresses, furniture padding, and thermal insulation. It is also one of the components (in non-blown form) of the fiber spandex.

In 1939, IG Farben filed a patent for "polyepoxide" or "epoxy". Epoxies are a class of thermoset plastic that form cross-links and "cure" when a catalyzing agent, or "hardener", is added. After the war they would come into wide use for coatings, "adhesives", and composite materials.

Composites using epoxy as a matrix include glass-reinforced plastic, where the structural element is glass fiber, and "carbon-epoxy composites", in which the structural element is carbon fiber. Fiberglass is now often used to build sport boats, and carbon-epoxy composites are an increasingly important structural element in aircraft, as they are lightweight, strong, and heat resistant.

Two chemists named Rex Whinfield and James Dickson, working at a small English company with the quaint name of the "Calico Printer's Association" in Manchester, developed "polyethylene terephthalate" (PET or PETE) in 1941, and it would be used for synthetic fibers in the postwar era, with names such as "polyester", "dacron", and "terylene".
PET is less gas-permeable than other low-cost plastics and so is a popular material for making bottles for Coca-Cola and other "fizzy drinks", since carbonation tends to attack other plastics, and for acidic drinks such as fruit or vegetable juices. PET is also strong and abrasion resistant, and is used for making mechanical parts, food trays, and other items that have to endure abuse. PET films are used as a base for recording tape.

One of the most impressive plastics used in the war, and a top secret, was "polytetrafluoroethylene" (PTFE), better known as "Teflon", which could be deposited on metal surfaces as a scratch-proof and corrosion-resistant, low-friction protective coating. The polyfluoroethylene surface layer created by exposing a polyethylene container to fluorine gas is very similar to Teflon.

A Du Pont chemist named Roy Plunkett discovered Teflon by accident in 1938. During the war, it was used in gaseous-diffusion processes to refine uranium for the atomic bomb, as the process was highly corrosive. By the early 1960s, Teflon "nonstick" frying pans were a hot item.

Teflon was later used to synthesize the breathable fabric "Gore-Tex", which can be used to build rain gear that in principle "breathes" to keep the wearer's moisture from building up. Gore-Tex is also used for surgical implants; Teflon strand is used to make dental floss; and Teflon mixed with fluorine compounds is used to make "decoy" flares dropped by aircraft to distract heat-seeking missiles.

After the war, the new plastics that had been developed entered the consumer mainstream in a flood. New manufacturing were developed, using various forming, molding, casting, and extrusion processes, to churn out plastic products in vast quantities. American consumers enthusiastically adopted the endless range of colorful, cheap, and durable plastic gimmicks being produced for new suburban home life.

One of the most visible parts of this plastics invasion was Earl Tupper's "Tupperware", a complete line of sealable polyethylene food containers that Tupper cleverly promoted through a network of housewives who sold Tupperware as a means of bringing in some money. The Tupperware line of products was well thought out and highly effective, greatly reducing spoilage of foods in storage. Thin-film "plastic wrap" that could be purchased in rolls also helped keep food fresh.

Another prominent element in 1950s homes was "Formica", a plastic laminate that was used to surface furniture and cabinetry. Formica was durable and attractive. It was particularly useful in kitchens, as it did not absorb, and could be easily cleaned of stains from food preparation, such as blood or grease. With Formica, a very attractive and well-built table could be built using low-cost and lightweight plywood with Formica covering, rather than expensive and heavy hardwoods like oak or mahogany.
Composite materials like fiberglass came into use for building boats and, in some cases, cars. Polyurethane foam was used to fill mattresses, and Styrofoam was used to line ice coolers and make float toys.

Plastics continue to be improved. General Electric introduced "lexan", a high-impact "polycarbonate" plastic, in the 1970s. Du Pont developed "Kevlar", an extremely strong synthetic fiber that was best known for its use in bullet-proof vests and combat helmets. Kevlar was so remarkable that Du Pont officials actually had to release statements to deny rumors that the company had received the recipe for it from space aliens.

8. The environment

Although plastics have had a remarkable impact globally, it has become increasingly obvious that there is a price to be paid for their use.

Plastics are durable and degrade very slowly. In some cases, burning plastic can release toxic fumes. Also, the manufacturing of plastics often creates large quantities of chemical pollutants. #3 - PVC (polyvinyl chloride), commonly used to package foods and liquids, ubiquitous in children's toys and teethers, plumbing and building materials, and in everything from cosmetics to shower curtains, contains numerous toxic chemicals called adipates and phthalates ("plasticizers"), which are used to soften brittle PVC into a more flexible form. Traces of these chemicals can leach out of PVC when it comes into contact with food. The World Health Organization's International Agency for Research on Cancer (IARC) has recognized the chemical used to make PVC - vinyl chloride - as a known human carcinogen. The European Union has banned the use of DEHP (di-2-ethylhexyl phthalate) - the most widely used plasticizer in PVC - in children's toys. #6 - PS (polystyrene) is one of the toxins the EPA (Environmental Protection Agency) monitors in America's drinking water. Its production also pollutes the atmosphere, destroying the ozone layer. Some compounds leaching from Styrofoam food containers interfere with hormone functions. It's a possible human carcinogen. # 7 - Other (usually polycarbonate (PC)) is a catchall group consists mainly of polycarbonates, whose primary building block is bisphenol A (BPA), a hormone disrupter that releases into food and liquid and acts like estrogen. Research in Environmental Health Perspectives finds that BPA (leached from the lining of tin cans, dental sealants and PC bottles) can increase body weight of lab animals' offspring, as well as impact hormone levels. A more recent animal study suggests that even low-level exposure to BPA results in insulin resistance, which can lead to inflammation and heart disease.

By the 1990s, plastic recycling programs were common in the United States and elsewhere. Thermoplastics can be remelted and reused, and thermoset plastics can be ground up and used as filler, though the purity of the material tends to degrade with each reuse cycle. There are methods by which plastics can be broken back down to a feedstock state.

To assist recycling of disposable items, the Plastic Bottle Institute of the Society of the Plastics Industry devised a now-familiar scheme to mark plastic bottles by plastic type. A recyclable plastic container using this scheme is marked with a triangle of three "chasing arrows", which enclose a number giving the plastic type:
Plastics type marks: the Resin identification code

1. PET (PETYE): Polyethylene Terephthalate - Commonly found on: 2-liter soft drink bottles, cooking oil bottles, peanut butter jars.
2. HDPE: High Density Polyethylene - Commonly found on: detergent bottles, milk jugs.
3. PVC: Polyvinyl Chloride - Commonly found on: plastic pipes, outdoor furniture, shrink-wrap, water bottles, salad dressing and liquid detergent containers.
4. LDPE: Low Density Polyethylene - Commonly found on: dry-cleaning bags, produce bags, trash can liners, food storage containers.
5. PP: Polypropylene - Commonly found on: bottle caps, drinking straws
6. PS: Polystyrene - Commonly found on: "Styrofoam peanuts," cups, plastic tableware, meat trays, take-away food clamshell containers
7. OTHER: Other - This plastic category, as its name of "other" implies, is any plastic other than the named #1 – #6, Commonly found on: certain kinds of food containers, Tupperware, and Nalgene bottles.

Unfortunately, recycling plastics has proven difficult. The biggest problem with plastic recycling is that it is difficult to automate the sorting of plastic waste, and so it is labor intensive. Typically, workers sort the plastic by looking at the resin identification code, though common containers like soda bottles can be sorted from memory. Other recyclable materials, such as metals, are easier to process mechanically. However, new mechanical sorting processes are being utilized to increase plastic recycling capacity and efficiency.

While containers are usually made from a single type and color of plastic, making them relatively easy to sort out, a consumer product like a cellular phone may have many small parts consisting of over a dozen different types and colors of plastics. In a case like this, the resources it would take to separate the plastics far exceed their value and the item is discarded. However, developments are taking place in the field of Active Disassembly, which may result in more consumer product components being re-used or recycled. Recycling certain types of plastics can be unprofitable, as well. For example, polystyrene is rarely recycled because it is usually not cost effective. These unrecyclable wastes can be disposed of in landfills, incinerated or used to produce electricity at waste-to-energy plants.

8.1. Biodegradable plastics

Research has been done on biodegradable plastics that break down with exposure to sunlight (e.g. ultra-violet radiation), water (or humidity), bacteria, enzymes, wind abrasion and some instances rodent pest or insect attack are also included as forms of biodegradation or environmental degradation. It is clear some of these modes of degradation will only work if the plastic is exposed at the surface, while other modes will only be effective if certain conditions are found in landfill or composting systems. Starch powder has been mixed with plastic as a filler to allow it to degrade more easily, but it still does not lead to complete breakdown of the plastic. Some
researchers have actually genetically engineered bacteria that synthesize a completely biodegradable plastic, but this material is expensive at present e.g. BP's Biopol. BASF make Ecoflex, a fully biodegradable polyester for food packaging applications. A potential disadvantage of biodegradable plastics is that the carbon that is locked up in them is released into the atmosphere as a greenhouse gas: carbon dioxide when they degrade, though if they are made from natural materials, such a vegetable crop derivatives or animal products, there is no net gain in carbon dioxide emissions, although concern will be for a worse greenhouse gas, methane release.

So far, these plastics have proven too costly and limited for general use, and critics have pointed out that the only real problem they address is roadside litter, which is regarded as a secondary issue. When such plastic materials are dumped into landfills, they can become "mummified" and persist for decades even if they are supposed to be biodegradable.

There have been some success stories. The Courtauld concern, the original producer of rayon, came up with a revised process for the material in the mid-1980s to produce "Tencel". Tencel has many superior properties over rayon, but is still produced from "biomass" feedstocks, and its manufacture is extraordinarily clean by the standards of plastic production.

The University of Illinois at Urbana has been working on developing biodegradable resins, sheets and films made with zein (corn protein).[1] Recently, however, a new type of biodegradable resin has made its debut in the United States, called Plastarch Material (PSM). It is heat, water, and oil resistant and sees a 70% degradation in 90 days. Biodegradable plastics based on polylactic acid (once derived from dairy products, now from cereal crops such as maize) have entered the marketplace, for instance as polylactates as disposable sandwich packs.

An alternative to starch based resins are additives such as Bio-Batch an additive that allows the manufacturers to make PE, PS, PP, PET, and PVC totally biodegradable in landfills where 94.8% of most plastics end up according to the EPA. According to their latest MSW report done in 2003, located under Municipal Solid Waste in the United States: 2003 Data Tables.

It is also possible that bacteria will eventually develop the ability to degrade plastics. This has already happened with nylon: two types of nylon eating bacteria, *Flavobacteria* and *Pseudomonas*, were found in 1975 to possess enzymes (nylonase) capable of breaking down nylon. While not a solution to the disposal problem, it is likely that bacteria will evolve the ability to use other synthetic plastics as well.

The latter possibility was in fact the subject of a cautionary novel by Kit Pedler and Gerry Davis (screenwriter), the creators of the Cybermen, re-using the plot of the first episode of their Doomwatch series. The novel, "*Mutant 59: The Plastic Eater*", written in 1971, is the story of what could happen if a bacterium were to evolve - or be artificially cultured - to eat plastics, and be let loose in a major city.
In the novel, the mutant bacterium is cultured by a lone scientist experimenting with the common germ *Bacillus prodigiosus*, with the intent of solving the world's plastic waste disposal problem; it is the 59th attempted variant (hence the novel's title), and is accidentally released when the scientist suffers a fatal cerebral haemorrhage, dropping a test-tube containing the bacteria into a sink as he collapses.

Needless to say, the consequences would be - and, in the novel, are - catastrophic; a modern city such as London would be paralysed if all its plastic suddenly began disappearing under bacterial action. If such a bacterium is ever developed or, worse, if it should spontaneously evolve - which can no longer be considered impossible - it would have to be rigidly controlled and not permitted to escape into the environment under any circumstances whatsoever.

9. Price, environment, and the future

One of the great appeals of plastics have been their low price as compared to other materials. However, in recent years the cost of plastics has been rising dramatically. The cause of the increase is the sharply rising cost of petroleum, the raw material that is chemically altered to form commercial plastics. As the cost of plastic hinges on the cost of petroleum, should petroleum prices continue to rise, so will the cost of plastic. In 2005, the higher price of plastic drove a number of plastic-toy manufacturers out of business.

Fears of dwindling petroleum supplies are becoming very real, with publications such as *USA Today* reporting that current oil reserves will only last 40 years. Alternate reserves such as oil shale and tar oil (tar sand) do exist, but the cost of production is much higher than with current sources. Nevertheless, the production cost of these alternatives and even more unconventional alternatives such as developing liquid hydrocarbons from coal or natural gas, is generally less than the high crude oil prices reached in 2005 and 2006. A more serious problem is that these unconventional petroleum sources may have even greater environmental impacts than conventional petroleum, as they require large amounts of energy to extract and process. In general, the biggest threat to the conventional plastics industry is likely to be environmental concerns about the production (and disposal) of petroleum and petroleum-based plastics, including the release of toxic and greenhouse gas pollutants.

Scientists are seeking cheaper and better alternatives to petroleum-based plastics, and many candidates are in laboratories all over the world. One promising alternative on the horizon is simple sugar.\[1\]

10. Common plastics and their uses

- **Polyethylene (PE)**
  - Wide range of inexpensive uses including supermarket bags, plastic bottles.
- **Polypropylene (PP)**
  - Food containers, appliances, car fenders ( bumpers).
- **Polystyrene (PS)**
  - Packaging foam, food containers, disposable cups, plates, cutlery, CD and cassette boxes.
11. Special-purpose plastics

Poly(methyl methacrylate) (PMMA) contact lenses, glazing (best known in this form by its various trade names around the world, e.g. "Perspex", "Oroglas", "Plexiglas"), fluorescent light diffusers, rear light covers for vehicles.

Polytetrafluoroethylene (PTFE) (trade name Teflon) Heat-resistant, low-friction coatings, used in things like "non-stick" surfaces for frying pans, plumber's tape and water slides.

Polyetheretherketone (PEEK) (Polyketone) Strong, chemical- and heat-resistant thermoplastic, biocompatibility allows for use in medical implant applications, aerospace mouldings. One of the most expensive commercial polymers.

Polyetherimide (PEI) (Ultem) A General Electric product, similar to PEEK.

Phenolics (PF) or (phenol formaldehydes) high modulus, relatively heat resistant, and excellent fire resistant polymer. Used for insulating parts in electrical fixtures, paper laminated products (e.g. "Formica"), thermally insulation foams. It is a thermosetting plastic, with the familiar trade name "Bakelite", that can be moulded by heat and pressure when mixed with a filler-like wood flour or can be cast in its unfilled liquid form or cast as foam, e.g. "Oasis". Problems include the probability of mouldings naturally being dark colours (red, green, brown), and as thermoset difficult to recycle. Urea formaldehyde (UF), one of the aminoplasts and used as multi-colorable alternative to Phenolics. Used as a wood adhesive (for plywood, chipboard, hardboard) and electrical switch housings.

Melamine formaldehyde (MF), one of the aminoplasts, and used a multi-colorable alternative to phenolics, for instance in mouldings (e.g. break-resistance alternatives
to ceramic cups, plates and bowls for children) and the decorated top surface layer of the paper laminates (e.g. "Formica").

Polyactic acid a biodegradable, thermoplastic, found converted into a variety of aliphatic polyesters derived from lactic acid which in turn can be made by fermentation of various agricultural products such as corn starch, once made from diary products.

Plastarch Material biodegradable and heat resistant, thermoplastic composed of modified corn starch.

12. Injection molding

Injection molding is a manufacturing technique for making parts from thermoplastic material in production. Molten plastic is injected at high pressure into a mold, which is the inverse of the product's shape. After a product is designed 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. Injection molding is the most common method of production, with some commonly made items including bottle caps and outdoor furniture. Injection molding typically is capable of an IT Grade of about 9-14.

![Injection molding mold](image)

Standard two plates tooling - Core and Cavity are inserts in a mold base - "Family mold" of 5 different parts

13. Materials

The most commonly used thermoplastic materials are polystyrene (low cost, lacking the strength and longevity of other materials), ABS or acrylonitrile butadiene styrene (a co-polymer or mixture of compounds used for everything from Lego parts to electronics housings), nylon (chemically resistant, heat resistant, tough and flexible - used for combs), polypropylene (tough and flexible - used for containers), polyethylene, and polyvinyl chloride or PVC (more common in extrusions as used for pipes, window frames, or as the insulation on wiring where it is rendered flexible by the inclusion of a high proportion of plasticiser).
14. Equipment

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

Injection molding machines, also known as presses, 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 generate. This pressure 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.

Injection molding machines can fasten the molds in either a horizontal or vertical position. The majority is horizontally oriented but vertical machines are used in some niche applications such as insert molding, allowing the machine to take advantage of gravity. There are many ways to fasten the tools to the platens, the most common being manual clamps (both halves are bolted to the platens); however hydraulic clamps (chocks are used to hold the tool in place) and magnetic clamps are also used. The magnetic and hydraulic clamps are used where fast tool changes are required.

Machines are classified primarily by the type of driving systems they use: hydraulic, electric, or hybrid. Hydraulic presses have historically been the only option available to molders until Nissei introduced the first all electric machine in 1983. The electric press, also known as Electric Machine Technology (EMT), reduces operation costs by cutting energy consumption and also addresses some of the environmental concerns surrounding the hydraulic press. Electric presses have been shown to be quieter, faster, and have a higher accuracy, however the machines are more expensive. Hybrid injection molding machines take advantage of the best features of both hydraulic and electric systems. Hydraulic machines are the predominant type in most of the world, with the exception of Japan.

Robotic arms are often used to remove the molded components; either by side or top entry, but it is more common for parts to drop out of the mold, through a chute and into a container.

15. Mold

Mold (Tool and/or Mold) is the common term used to describe the production tooling used to produce plastic parts in injection molding.

Traditionally, molds have been expensive to manufacture. They were usually only used in mass production where thousands of parts were being produced. Molds are typically constructed from hardened steel, pre-hardened steel, aluminum, and/or
beryllium-copper alloy. The choice of material to build a mold is primarily one of economics. Steel molds generally 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 steel hardness is typically 38-45 on the Rockwell-C scale. Hardened steel molds are generally vacuum hardened or age hardened 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 hundreds or even tens of thousands of parts. Beryllium copper is used in areas of the mold which require fast heat removal or areas that see the most shear heat generated. High performance alloys such as Moldmax have also been developed especially for optimum heat transfer. Such alloys are considered in mold construction when conventional heat removal methods are unsuitable or when cycle time is a critical consideration.

Considerable thought is put into the design of molded parts and their molds, to ensure that the parts will not be trapped in the mold, that the molds can be completely filled before the molten resin solidifies, to compensate for material shrinkage, and to minimize imperfections in the parts.

15.1. Design

Molds separate into at least two halves (called the core and the cavity) to permit the part to be extracted. In general the shape of a part must not cause it to be locked into the mold. For example, sides of objects typically cannot be parallel with the direction of draw (the direction in which the core and cavity separate from each other). They are angled slightly (draft), and examination of most plastic household objects will reveal this. Parts that are "bucket-like" tend to shrink onto the core while cooling, and after the cavity is pulled away. Pins are the most popular method of removal from the core, but air ejection, and stripper plates can also be used depending on the application. Most ejection plates are found on the moving half of the tool, but they can be placed on the fixed half.

More complex parts are formed using more complex molds, which may have movable sections called slides which are inserted into the mold to form features that cannot be formed using only a core and a cavity. Slides are then withdrawn to allow the part to be released. 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.

2-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 can be achieved by having pairs of identical cores and pairs of different cavities within the mold. After injection of the first material, the component is rotated on the core from the one cavity to another. The second cavity differs from the first in that the detail for the second material is included. The second material is then injected into the additional cavity detail before the completed part is ejected from the mold. Common applications include the "soft-grip" toothbrush, the freelancer grab handles are formed this way.
The core and cavity, along with injection and cooling hoses form the mold tool. While large tools are very heavy (up to 60t), they can be hoisted into molding machines for production and removed when molding is complete or the tool needs repairing.

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 referred to as cavitation. A tool with one impression will often be called a single cavity (impression) tool. A mold with 2 or more cavities of the same parts will likely be referred to as multiple cavity (impressions) tooling. Some extremely high production volume molds (like those for bottle caps) can have over 128 cavities (impressions).

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 not the same but often part of a family of parts (to be used in the same product in example).

### 15.2. Machining

Molds are built through two main methods: standard machining and EDM machining. 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 which 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 steel, 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 erosion of the mold surface in the inverse shape of the electrode.

### 15.3. 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.

### 16. Injection process

![Small injection molder showing hopper, nozzle and die area](image)
### 16.1. Injection Molding Cycle

**The basic injection cycle is as follows:** Mold close - injection carriage forward - inject plastic - metering - carriage retract - mold open - eject part(s)

The molds are closed shut by hydraulics or electric, and the heated plastic is forced by the pressure of the injection screw to take the shape of the mold. Some machines are run by electric motors instead of hydraulics or a combination of both. The water-cooling channels then assist in cooling the mold and the heated plastic solidifies into the part. Improper cooling can result in distorted molding or one that is burnt. The cycle is completed when the mold opens and the part is ejected with the assistance of ejector pins within the mold.

The resin, or raw material for injection molding, is usually in pellet or granule form, and is melted by heat and shearing forces shortly before being injected into the mold. Resin pellets are poured into the feed hopper, a large open bottomed container, which feeds the granules down to the screw. The screw is rotated by a motor, feeding pellets up the screw's grooves. The depth of the screw flights decreases towards the end of the screw nearest the mold, compressing the heated plastic. As the screw rotates, the pellets are moved forward in the screw and they undergo extreme pressure and friction which generates most of the heat needed to melt the pellets. Heaters on either side of the screw assist in the heating and temperature control during the melting process.

The channels through which the plastic flows toward the chamber will also solidify, forming an attached frame. This frame is composed of the sprue, which is the main channel from the reservoir of molten resin, parallel with the direction of draw, and runners, which are perpendicular to the direction of draw, and are used to convey molten resin to the gate(s), or point(s) of injection. The sprue and runner system can be cut or twisted off and recycled, sometimes being granulated next to the mold machine. Some molds are designed so that the part is automatically stripped through action of the mold.

### 16.2. 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 should start with a small shot weight and fill gradually until it 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 has occurred, then 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.
### 16.3. Molding defects

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

<table>
<thead>
<tr>
<th>Molding Defects</th>
<th>Alternative name</th>
<th>Descriptions</th>
<th>Causes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blister</td>
<td>Blistering</td>
<td>Raised or layered zone on surface of the part</td>
<td>Tool or material is too hot, often caused by a lack of cooling around the tool or a faulty heater</td>
</tr>
<tr>
<td>Burn Marks</td>
<td>Air Burn/Gas Burn</td>
<td>Localized burnt zone (often in the yellow/brown tones)</td>
<td>Tool lacks venting, injection speed is too high</td>
</tr>
<tr>
<td>Color Streaks</td>
<td></td>
<td>Localized change of color</td>
<td>Masterbatch isn't mixing properly, or the material has run out and it's starting to come through as natural only</td>
</tr>
<tr>
<td>Delamination</td>
<td></td>
<td>Thin mica like layers formed in part wall</td>
<td>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</td>
</tr>
<tr>
<td>Flash</td>
<td>Burrs</td>
<td>Excess material in thin layer exceeding normal part geometry</td>
<td>Tool damage, too much injection speed/material injected</td>
</tr>
<tr>
<td>Embedded</td>
<td>Embedded</td>
<td>Foreign particle</td>
<td>Particles on the tool surface,</td>
</tr>
<tr>
<td>Part</td>
<td>Description</td>
<td>Cause</td>
<td>Cause Details</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>-------</td>
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</tr>
<tr>
<td><strong>Flow marks</strong></td>
<td>Directionally &quot;off tone&quot; wavy lines or patterns</td>
<td>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)</td>
<td></td>
</tr>
<tr>
<td><strong>Jetting</strong></td>
<td>Deformed part by turbulent flow of material</td>
<td>Poor tool design</td>
<td></td>
</tr>
<tr>
<td><strong>Silver streaks</strong></td>
<td>Circular pattern around gate caused by hot gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sink Marks</strong></td>
<td>Localized depression (In thicker zones)</td>
<td>Holding time/pressure too low, cooling time too low, with sprueless hot runners this can also be caused by the gate temperature being set too high</td>
<td></td>
</tr>
<tr>
<td><strong>Short shot</strong></td>
<td>Non-Fill / Short mold</td>
<td>Partial part</td>
<td>Lack of material, injection speeds too slow</td>
</tr>
<tr>
<td><strong>Splay Marks</strong></td>
<td>Circular pattern around gate caused by hot gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stringiness</strong></td>
<td>String like remain from previous shot transfer in new shot</td>
<td>Gate hasn't frozen off</td>
<td></td>
</tr>
<tr>
<td><strong>Voids</strong></td>
<td>Empty space within part (Air pocket)</td>
<td>Lack of holding pressure (holding pressure is used to pack out the part during the holding time)</td>
<td></td>
</tr>
</tbody>
</table>
### 17. Ceramic Materials

The word **ceramic** is derived from the Greek word κεραμικός (keramikos). The term covers inorganic non-metallic materials whose formation is due to the action of heat. Up until the 1950s or so, the most important of these were the traditional clays, made into pottery, bricks, tiles and are like, along with cements and glass. Clay based ceramics are described in the article on pottery. A composite material of ceramic and metal is known as cermet. The word ceramic can be an adjective, and can also be used as a noun to refer to a ceramic material, or a product of ceramic manufacture. Ceramics is a singular noun referring to the art of making things out of ceramic materials.

Many ceramic materials are hard, porous and brittle. The study and development of ceramics includes methods to mitigate problems associated with these characteristics, and to accentuate the strengths of the materials as well as to investigate novel applications.

The American Society for Testing and Materials (ASTM) defines a ceramic article as "an article having a glazed or unglazed body of crystalline or partly crystalline structure, or of glass, which body is produced from essentially inorganic, non-metallic substances and either is formed from a molten mass which solidifies on cooling, or is formed and simultaneously or subsequently matured by the action of the heat."[^1]

### Types of ceramic materials

For convenience ceramic products are usually divided into four sectors, and these are shown below with some examples:

- **Structural**, including bricks, pipes, floor and roof tiles
- **Refractories**, such as kiln linings, gas fire radiants, steel and glass making crucibles
- **Whitewares**, including tableware, wall tiles, decorative art objects and sanitary ware
- **Technical**, is also known as Engineering, Advanced, Special, and in Japan, Fine Ceramics. Such items include tiles used in the Space Shuttle program, gas burner nozzles, ballistic protection, nuclear fuel uranium oxide pellets, bio-

<table>
<thead>
<tr>
<th>Weld line</th>
<th>Knit Line</th>
<th>Discolored line where two flow fronts meet</th>
<th>Mold/material temperatures set too low (the material is cold when they meet, so they don't bond)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warping</td>
<td>Twisting</td>
<td>Distorted part</td>
<td>Cooling is too short, material is too hot, lack of cooling around the tool, incorrect water temperatures (the parts bow inwards towards the cool side of the tool)</td>
</tr>
</tbody>
</table>

[^1]: American Society for Testing and Materials (ASTM)
medical implants, jet engine turbine blades, and missile nose cones. Frequently the raw materials do not include clays.

18. Examples of structural ceramics

- Construction bricks.
- Floor and roof tiles.
- Sewage pipes

19. Examples of whiteware ceramics

- Bone china
- Earthenware, which is often made from clay, quartz and feldspar.
- Porcelain, which are often made from kaolin
- Stoneware

20. Classification of technical ceramics

Technical ceramics can also be classified into three distinct material categories:

- Oxides: Alumina, zirconia
- Non-oxides: Carbides, borides, nitrides, silicides
- Composites: Particulate reinforced, combinations of oxides and non-oxides.

Each one of these classes can develop unique material properties

20.1. Examples of technical ceramics

- Barium titanate (often mixed with strontium titanate) displays ferroelectricity, meaning that its mechanical, electrical, and thermal responses are coupled to one another and also history-dependent. It is widely used in electromechanical transducers, ceramic capacitors, and data storage elements. Grain boundary conditions can create PTC effects in heating elements.
- Bismuth strontium calcium copper oxide, a high-temperature superconductor
- Boron carbide (B₄C), which is used in ceramic plates in some personnel, helicopter and tank armor.
- Boron nitride is structurally isoelectronic to carbon and takes on similar physical forms: a graphite-like one used as a lubricant, and a diamond-like one used as an abrasive.
- Ferrite (Fe₃O₄), which is ferrimagnetic and is used in the magnetic cores of electrical transformers and magnetic core memory.
- Lead zirconate titanate is another ferroelectric material.
- Magnesium diboride (MgB₂), which is an unconventional superconductor.
- Silicon carbide (SiC), which is used as a susceptor in microwave furnaces, a commonly used abrasive, and as a refractory material.
- Silicon nitride (Si₃N₄), which is used as an abrasive powder.
- Steatite is used as an electrical insulator.
21. Properties of ceramics

21.1. Mechanical properties

Ceramic materials are usually ionic or covalently-bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before any plastic deformation takes place, which results in poor toughness in these materials. Additionally, because these materials tend to be porous, the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength. These combine to give catastrophic failures, as opposed to the normally much more gentle failure modes of metals.

These materials do show plastic deformation. However, due to the rigid structure of the crystalline materials, there are very few available slip systems for dislocations to move, and so they deform very slowly. With the non-crystalline (glassy) materials, viscous flow is the dominant source of plastic deformation, and is also very slow. It is therefore neglected in many applications of ceramic materials.

21.2. Electrical properties

21.2.1. Semiconductors

There are a number of ceramics that are semiconductors. Most of these are transition metal oxides that are II-VI semiconductors, such as zinc oxide.

While there is talk of making blue LEDs from zinc oxide, ceramicists are most interested in the electrical properties that show grain boundary effects.

One of the most widely used of these is the varistor. These are devices that exhibit the property that resistance drops sharply at a certain threshold voltage. Once the voltage across the device reaches the threshold, there is a breakdown of the electrical structure in the vicinity of the grain boundaries, which results in its electrical resistance dropping from several megohms down to a few hundred ohms. The major advantage of these is that they can dissipate a lot of energy, and they self reset — after the voltage across the device drops below the threshold, its resistance returns to being high.
This makes them ideal for surge-protection applications. As there is control over the threshold voltage and energy tolerance, they find use in all sorts of applications. The best demonstration of their ability can be found in electrical substations, where they are employed to protect the infrastructure from lightning strikes. They have rapid response, are low maintenance, and do not appreciably degrade from use, making them virtually ideal devices for this application.

Semiconducting ceramics are also employed as gas sensors. When various gases are passed over a polycrystalline ceramic, its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.

### 21.2.2. Superconductivity

Under some conditions, such as extremely low temperature, some ceramics exhibit superconductivity. The exact reason for this is not known, but there are two major families of superconducting ceramics.

### 21.2.3. Ferroelectricity and supersets

Piezoelectricity, a link between electrical and mechanical response, is exhibited by a large number of ceramic materials, including the quartz used to measure time in watches and other electronics. Such devices use both properties of piezoelectrics, using electricity to produce a mechanical motion (powering the device) and then using this mechanical motion to produce electricity (generating a signal). The unit of time measured is the natural interval required for electricity to be converted into mechanical energy and back again.

The piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. These materials can be used to interconvert between thermal, mechanical, and/or electrical energy; for instance, after synthesis in a furnace, a pyroelectric crystal allowed to cool under no applied stress generally builds up a static charge of thousands of volts. Such materials are used in motion sensors, where the tiny rise in temperature from a warm body entering the room is enough to produce a measurable voltage in the crystal.

In turn, pyroelectricity is seen most strongly in materials which also display the ferroelectric effect, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. Pyroelectricity is also a necessary consequence of ferroelectricity. This can be used to store information in ferroelectric capacitors, elements of ferroelectric RAM.

The most common such materials are lead zirconate titanate and barium titanate. Aside from the uses mentioned above, their strong piezoelectric response is exploited in the design of high-frequency loudspeakers, transducers for sonar, and actuators for atomic force and scanning tunneling microscopes.

### 21.2.4. Positive thermal coefficient

Increases in temperature can cause grain boundaries to suddenly become insulating in some semiconducting ceramic materials, mostly mixtures of heavy metal titanates. The critical transition temperature can be adjusted over a wide range by variations in...
chemistry. In such materials, current will pass through the material until joule heating brings it to the transition temperature, at which point the circuit will be broken and current flow will cease. Such ceramics are used as self-controlled heating elements in, for example, the rear-window defrost circuits of automobiles.

At the transition temperature, the material's dielectric response becomes theoretically infinite. While a lack of temperature control would rule out any practical use of the material near its critical temperature, the dielectric effect remains exceptionally strong even at much higher temperatures. Titanates with critical temperatures far below room temperature have become synonymous with "ceramic" in the context of ceramic capacitors for just this reason.

22. Classification of ceramics

Non-crystalline ceramics: Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in a state of toffee-like viscosity, by methods such as blowing to a mold. If later heat-treatments cause this class to become partly crystalline, the resulting material is known as a glass-ceramic.

Crystalline ceramics: Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories - either make the ceramic in the desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body. Ceramic forming techniques include shaping by hand (sometimes including a rotation process called "throwing"), slip casting, tape casting (used for making very thin ceramic capacitors, etc.), injection molding, dry pressing, and other variations. (See also Ceramic forming techniques. Details of these processes are described in the two books listed below.) A few methods use a hybrid between the two approaches.

22.1. In situ manufacturing

The most common use of this method is in the production of cement and concrete. Here, the dehydrated powders are mixed with water. This starts hydration reactions, which result in long, interlocking crystals forming around the aggregates. Over time, these result in a solid ceramic.

The biggest problem with this method is that most reactions are so fast that good mixing is not possible, which tends to prevent large-scale construction. However, small-scale systems can be made by deposition techniques, where the various materials are introduced above a substrate, and react and form the ceramic on the substrate. This borrows techniques from the semiconductor industry, such as chemical vapour deposition, and is very useful for coatings.

These tend to produce very dense ceramics, but do so slowly.

22.2. Sintering-based methods

The principles of sintering-based methods is simple. Once a roughly held together object (called a "green body") is made, it is baked in a kiln, where diffusion processes cause the green body to shrink. The pores in the object close up, resulting in a
denser, stronger product. The firing is done at a temperature below the melting point of the ceramic. There is virtually always some porosity left, but the real advantage of this method is that the green body can be produced in any way imaginable, and still be sintered. This makes it a very versatile route.

There are thousands of possible refinements of this process. Some of the most common involve pressing the green body to give the densification a head start and reduce the sintering time needed. Sometimes organic binders such as polyvinyl alcohol are added to hold the green body together; these burn out during the firing (at 200–350°C). Sometimes organic lubricants are added during pressing to increase densification. It is not uncommon to combine these, and add binders and lubricants to a powder, then press. (The formulation of these organic chemical additives is an art in itself. This is particularly important in the manufacture of high performance ceramics such as those used by the billions for electronics, in capacitors, inductors, sensors, etc. The specialized formulations most commonly used in electronics are detailed in the book "Tape Casting," by R.E. Mistler, et al., Amer. Ceramic Soc. [Westerville, Ohio], 2000.) A comprehensive book on the subject, for mechanical as well as electronics applications, is "Organic Additives and Ceramic Processing," by D. J. Shanefield, Kluwer Publishers [Boston], 1996.

A slurry can be used in place of a powder, and then cast into a desired shape, dried and then sintered. Indeed, traditional pottery is done with this type of method, using a plastic mixture worked with the hands.

If a mixture of different materials is used together in a ceramic, the sintering temperature is sometimes above the melting point of one minor component - a liquid phase sintering. This results in shorter sintering times compared to solid state sintering.

23. Other applications of ceramics

In the early 1980s, Toyota researched production of an adiabatic ceramic engine which can run at a temperature of over 6000 °F (3300 °C). Ceramic engines do not require a cooling system and hence allow a major weight reduction and therefore greater fuel efficiency. Fuel efficiency of the engine is also higher at high temperature, as shown by Carnot's theorem. In a conventional metallic engine, much of the energy released from the fuel must be dissipated as waste heat in order to prevent a meltdown of the metallic parts.

Despite all of these desirable properties, such engines are not in production because the manufacturing of ceramic parts in the requisite precision and durability is difficult. Imperfection in the ceramic leads to cracks, which can lead to potentially dangerous equipment failure. Such engines are possible in laboratory settings, but mass-production is unfeasible with current technology.
Work is being done in developing ceramic parts for gas turbine engines. Currently, even blades made of advanced metal alloys used in the engines' hot section require cooling and careful limiting of operating temperatures. Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel.

Ceramics are used in the manufacture of knives. The blade of the ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.

Since the late 1990s, highly specialized ceramics, usually based on boron carbide, formed into plates and lined with Spectra, have been used in ballistic armored vests to repel large-caliber rifle fire. Such plates are known commonly as small-arms protective inserts (SAPI). Very similar technology is used to protect cockpits of some military airplanes, because of the low weight of the material.

Recently, there have been advances in ceramics which include bio-ceramics, such as dental implants and synthetic bones. Hydroxyapatite, the natural mineral component of bone, has been made synthetically from a number of biological and chemical sources and can be formed into ceramic materials. Orthopedic implants made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions. Because of this, they are of great interest for gene delivery and tissue engineering scaffolds. Most hydroxyapatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers. They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials. Work is being done to make strong-fully dense nano crystalline hydroxapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic natural bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones.

### 24. Ceramic forming techniques

**Ceramic forming techniques** are ways of forming ceramic shapes. This can be used to make everyday tableware, such as a teapot, to engineering ceramics such as computer parts.

There are many forming techniques to make ceramics, but one example is slipcasting. This is where slip, liquid clay, is poured into a plaster of Paris mold. The water in the slip is drawn out of the slip, leaving an inside layer of solid clay. When this is thick enough, the excess slip can be removed from the mold. When dry, the solid clay can then also be removed. The slip used in slip casting is often liquefied with a substance that reduces the need for additional water to soften the slip; this prevents excessive shrinkage which occurs when a piece containing a lot of water dries.

The original mold for a slip cast, as well as the pieces themselves in many individual works of ceramics, can be thrown on a potter's wheel. The advantage of the wheel in forming ceramic vessels is that its rotation allows symmetrical adjustments to the piece, resulting in a uniform and balanced pot. Throwing, as forming ceramics on a
wheel is called, consists of three or four steps. First, the clay must be centered on the
wheel. (The pot will likely be ruined if this step is completed improperly or if the piece
is allowed to become uncentered at any point in the process.) Second, the center
must be opened. Third, the clay forming the walls of the pot must be squeezed gently
in order to force the clay upwards, causing the pot to become taller. Fourth (this step
is omitted entirely in the creation of simple objects such as cylinders and bowls) the
pot must be coaxed into the desired shape by carefully pushing in the appropriate
direction. A finished pot is cut off the wheel with a wire tool. "Feet" may be trimmed
into the bottoms of some pieces; this is accomplished by allowing the thrown pot to
dry to leather hard and then centering it upside down on the wheel, then carving into
the middle of the base of the piece with a trimming tool.

There are also several traditional techniques of handbuilding, such as pinching, soft
slab, hard slab, and coil construction.

Other techniques involve threading animal or artificial wool fibre through paperclay
slip, to build up layers of material. The result can be wrapped over forms or cut, dried
and later joined with liquid and soft paperclay.

When forming very thin sheets of ceramic material, "tape casting" is commonly used. This
involves pouring the slip (which contains a polymer "binder" to give it strength) onto a moving carrier belt, and then passing it under a stationary "doctor blade" to adjust the thickness. The moving slip is then air dried, and the "tape" thus formed is peeled off the carrier belt, cut into rectangular shapes, and processed further. As many as 100 tape layers, alternating with conductive metal powder layers, can be stacked up. These are then sintered ("fired") to remove the polymer and thus make "multilayer" capacitors, sensors, etc. According to D. W. Richerson of the American Ceramic Society, more than a billion of such capacitors are manufactured every day.
(About 100 are in a typical cellular telephone, and about a thousand in a typical
automobile.) Details of the binder systems and defect-free forming techniques are
described in "Organic Additives And Ceramic Processing" by D. J. Shanefield

When forming technical ceramic materials from dry powders prepared for processing,
the method of forming into the shape required depends upon the method of material
preparation and size and shape of the part to be formed. Materials prepared for dry
powder forming are most commonly formed by "dry" pressing in mechanical or
hydraulic powder compacting presses selected for the necessary force and powder
fill depth. Dry powder is automatically discharged into the non-flexible steel or
tungsten carbide insert in the die and punches then compact the powder to the shape
of the die. If the part is to be large and unable to have pressure transmit suitably for a
uniform pressed density then isostatic pressing may be used. When isostatically
pressed the powder takes the shape of a flexible membrane acting as the mold,
forming the shape and size of the pressed powder. Isostatic presses can be either
high speed, high output type of automatic presses for such parts as ceramic
insulators for spark plugs or sand blast nozzles, or slower operating "wet bag"
presses that are much more manual in operation but suitable particularly for large
machinable blanks or blanks that will be cut or otherwise formed in secondary
operations to the final shape.
If technical ceramic parts are needed where the length to diameter ratio is very large, extrusion may be used. There are two types of ceramic extruders one being piston type with hydraulic force pushing a ram that in turn is pushing the ceramic through the loaded material cylinder to and through the die which forms the extrudate. The second type of extruder is a screw, or auger, type where a screw turns forcing the material to and through the die which again shapes the part. In both types of extrusion the raw material must be plasticized to allow and induce the flow of the material in the process.

Complex technical ceramic parts are commonly formed using either the injection molding process or a process known as "hot wax molding" both of which rely upon heat sensitive plasticizers to allow flow of the material into a die which forms the part. The part is then quickly cooled for removal from the die. The injection molding process is much like injection molding of plastic materials using various polymers for plasticizing while the hot wax molding process largely uses paraffin wax.

There are also many more techniques, such as gel casting and injection molding that are often used to create engineering ceramics.

25. References


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