Materials Degradation in Materials Science

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Chapter 1

Corrosion

Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as rusting. This type of damage typically produces oxide(s) and/or salt(s) of the original metal. Corrosion can also refer to other materials than metals, such as ceramics or polymers, although in this context, the term degradation is more common.

In other words, corrosion is the wearing away of metals due to a chemical reaction.

Many structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate-conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

Rust, the most familiar example of corrosion.

Volcanic gases have sped the corrosion of this abandoned mining machinery.

Corrosion on exposed metal.

Galvanic corrosion

Galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. In order for galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. This effects a galvanic couple where the more active metal corrodes at an accelerated rate and the more noble metal corrodes at a retarded rate. When immersed, neither metal would normally corrode as quickly without the electrically conductive connection (usually via a wire or direct contact). Galvanic corrosion is often utilized in sacrificial anodes. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures, such as pipelines or docked naval ships. Galvanic corrosion is of major interest to the marine industry and also anywhere water can contact pipes or metal structures.

Factors such as relative size of anode (smaller is generally less desirable), types of metal, and operating conditions (temperature, humidity, salinity, etc.) will affect galvanic corrosion. The surface area ratio of the anode and cathode will directly affect the corrosion rates of the materials.

Galvanic series

In a given sea environment (one standard medium is aerated, room-temperature seawater), one metal will be either more *noble* or more *active* than the next, based on how strongly its ions are bound to the surface. Two metals in electrical contact share the same electrons, so that the tug-of-war at each surface is translated into a competition for free electrons between the two materials. The noble metal will tend to take electrons from the active one, while the electrolyte hosts a flow of ions in the same direction. The resulting mass flow or electrical current can be measured to establish a hierarchy of materials in the medium of interest. This hierarchy is called a *galvanic series*, and can be a very useful in predicting and understanding corrosion.

Resistance to corrosion

Some metals are more intrinsically resistant to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. If a more susceptible material is used, many techniques can be applied during an item's manufacture and use to protect its materials from damage.

Intrinsic chemistry

Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavorable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth, and is a large part of their intrinsic value. More common "base" metals can only be protected by more temporary means.

Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favorable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

Passivation

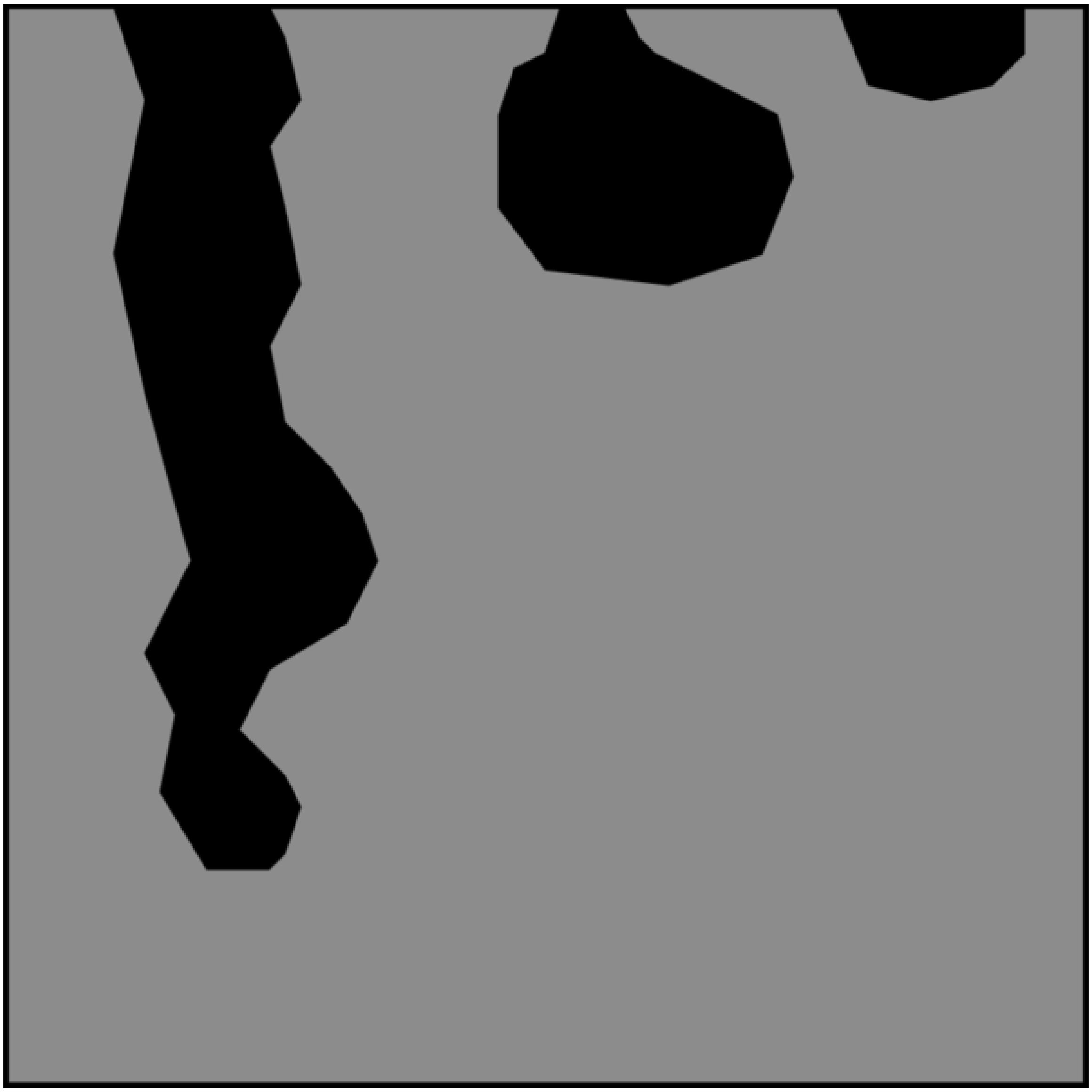
Given the right conditions, a thin film of corrosion products can form on a metal's surface spontaneously, acting as a barrier to further oxidation. When this layer stops growing at less than a micrometre thick under the conditions that a material will be used in, the phenomenon is known as passivation (rust, for example, usually grows to be much thicker, and so is not considered passivation, because this mixed oxidized layer is not protective). While this effect is in some sense a property of the material, it serves as an indirect kinetic barrier: the reaction is often quite rapid unless and until an impermeable layer forms. Passivation in air and water at moderate pH is seen in such materials as aluminium, stainless steel, titanium, and silicon.

These conditions required for passivation are specific to the material. The effect of pH is recorded using Pourbaix diagrams, but many other factors are influential. Some conditions that inhibit passivation include: high pH for aluminium, low pH or the presence of chloride ions for stainless steel, high temperature for titanium (in which case the oxide dissolves into the metal, rather than the electrolyte) and fluoride ions for silicon. On the other hand, sometimes unusual conditions can bring on passivation in materials that are normally unprotected, as the alkaline environment of concrete does for steel rebar. Exposure to a liquid metal such as mercury or hot solder can often circumvent passivation mechanisms.

Corrosion in passivated materials

Passivation is extremely useful in alleviating corrosion damage, but care must be taken not to trust it too thoroughly. Even a high-quality alloy will corrode if its ability to form a passivating film is hindered. Because the resulting modes of corrosion are more exotic and their immediate results are less visible than rust and other bulk corrosion, they often escape notice and cause problems among those who are not familiar with them.

Pitting corrosion



The scheme of pitting corrosion

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which compete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause *corrosion pits* of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an auto-catalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated alloys, but it can be prevented by control of the alloy's environment.

Weld decay and knifeline attack

Stainless steel can pose special corrosion challenges, since its passivating behavior relies on the presence of a minor alloying component (Chromium, typically only 18%). Due to the elevated temperatures of welding or during improper heat treatment, chromium carbides can form in the grain boundaries of stainless alloys. This chemical reaction robs the material of chromium in the zone near the grain boundary, making those areas much less resistant to corrosion. This creates a galvanic couple with the well-protected alloy nearby, which leads to *weld decay* (corrosion of the grain boundaries near welds) in highly corrosive environments. Special alloys, either with low carbon content or with added carbon "getters" such as titanium and niobium (in types 321 and 347, respectively), can prevent this effect, but the latter require special heat treatment after welding to prevent the similar phenomenon of *knifeline attack*. As its name applies, this is limited to a small zone, often only a few micrometres across, which causes it to proceed more rapidly. This zone is very near the weld, making it even less noticeable[1].

Crevice corrosion

Crevice corrosion is a localized form of corrosion occurring in spaces to which the access of the working fluid from the environment is limited and a concentration cell, areas with different oxygen concentration, will take place with consequent high corrosion rate . These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Microbial corrosion

Microbial corrosion, or bacterial corrosion, is a corrosion caused or promoted by microorganisms, usually chemoautotrophs. It can apply to both metals and non-metallic materials, in both the presence and lack of oxygen. Sulfate-reducing bacteria are common in lack of oxygen; they produce hydrogen sulfide, causing sulfide stress cracking. In presence of oxygen, some bacteria directly oxidize iron to iron oxides and hydroxides, other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion. Concentration cells can form in the deposits of corrosion products, causing and enhancing galvanic corrosion.

Accelerated Low Water Corrosion (ALWC) is a particularly aggressive form of MIC that affects steel piles in seawater near the low water tide mark. It is characterised by an orange sludge, which smells of Hydrogen Sulphide when treated with acid. Corrosion rates can be very high and design corrosion allowances can soon be exceeded leading to premature failure of the steel pile. Piles that have been coating and have cathodic protection installed at the time of construction are not susceptible to ALWC. For unprotected piles, sacrificial anodes can be installed local to the affected areas to inhibit the corrosion or a complete retrofitted sacrificial anode system can be installed. Affected areas can also be treated electrochemically by using an electrode to first produce chlorine to kill the bacteria, and then to produced a calcareous deposit, which will help shield the metal from further attack.

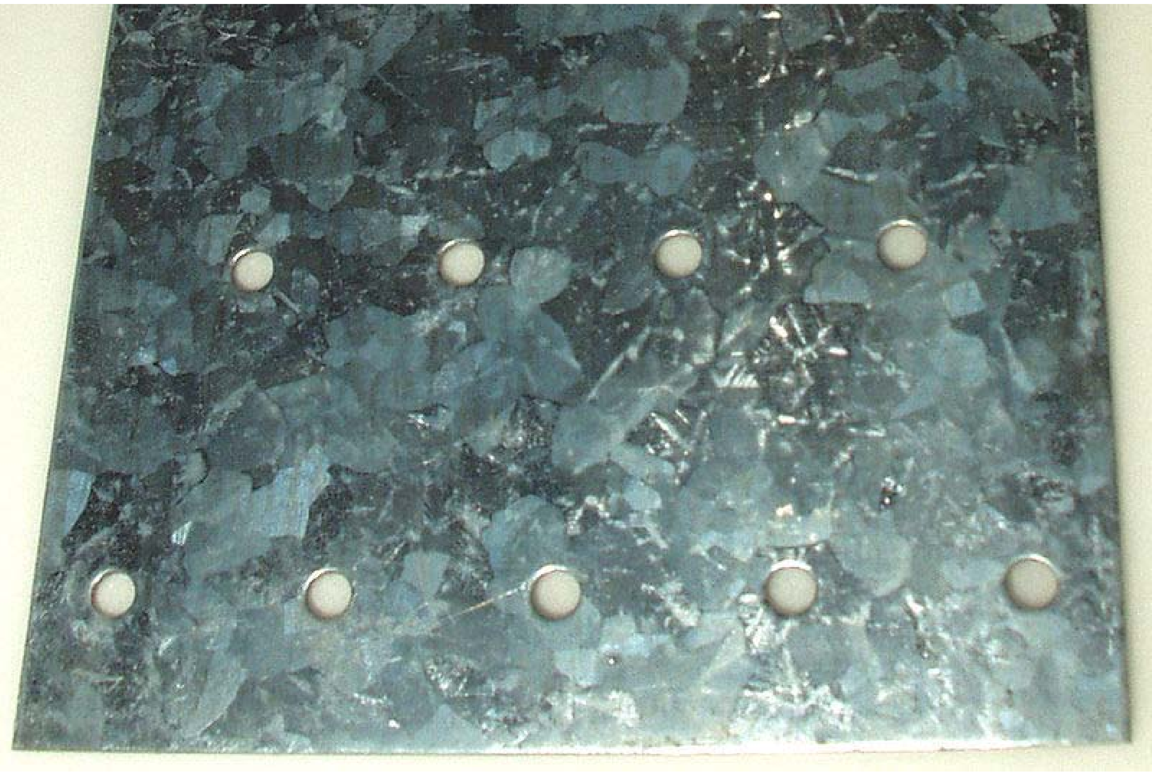
High temperature corrosion

High temperature corrosion is chemical deterioration of a material (typically a metal) under very high temperature conditions. This non-galvanic form of corrosion can occur when a metal is subject to a high temperature atmosphere containing oxygen, sulfur or other compounds capable of oxidising (or assisting the oxidation of) the material concerned. For example, materials used in aerospace, power generation and even in car engines have to resist sustained periods at high temperature in which they may be exposed to an atmosphere containing potentially highly corrosive products of combustion.

The products of high temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperature in hostile conditions. Such high temperature corrosion products in the form of compacted oxide layer glazes have also been shown to prevent or reduce wear during high temperature sliding contact of metallic (or metallic and ceramic) surfaces.

Methods of protection from corrosion

Surface treatments



Galvanized surface

Applied coatings

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the (often cheaper, tougher, and/or easier-to-process) structural material. Aside from cosmetic and manufacturing issues, there are tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with a more active metal such as zinc or cadmium. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel decks and waterfront applications. Flexible polyurethane coatings, like Durabak-M26 for example, can provide an anti-corrosive seal with a highly durable slip resistant membrane. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary.

Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These form an electrically insulating and/or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods obviously make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially-designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

This figure-8 descender is annodized with a yellow finish. Climbing equipment is available in a wide range of anodized colors.

Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores several nanometers wide appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area. Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas that the surface will come into regular contact with the elements. Whilst being resilient, it must be cleaned frequently. If left without cleaning Panel Edge Staining will naturally occur.

Controlled permeability formwork

Controlled permeability formwork (CPF) is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete placement, . CPF has been used in environments to combat the effects of carbonation, chlorides, frost and abrasion.

Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

Sacrificial anode protection

Sacrificial anode in the hull of a ship.

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

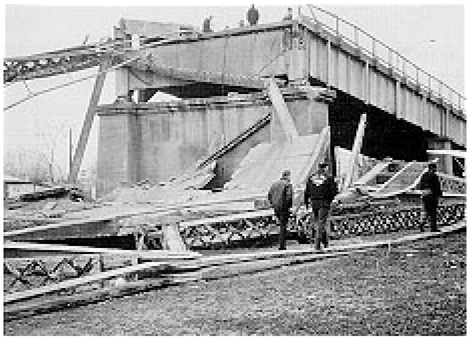
Impressed current cathodic protection

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (such as a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires.

Anodic protection

Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g., stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, e.g., solutions of sulfuric acid.

Economic impact



The collapsed Silver Bridge, as seen from the Ohio side

The US Federal Highway Administration released a study, entitled *Corrosion Costs and Preventive Strategies in the United States,* in 2002 on the direct costs associated with metallic corrosion in nearly every U.S. industry sector. The study showed that for 1998 the total annual estimated direct cost of corrosion in the U.S. was approximately $276 billion (approximately 3.2% of the US gross domestic product).

Rust is one of the most common causes of bridge accidents. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts. It was the cause of the collapse of the Mianus river bridge in 1983, when the bearings rusted internally and pushed one corner of the road slab off its support.

Three drivers on the roadway at the time died as the slab fell into the river below. The following NTSB investigation showed that a drain in the road had been blocked for road re-surfacing, and had not been unblocked so that runoff water penetrated the support hangers. It was also difficult for maintenance engineers to see the bearings from the inspection walkway. Rust was also an important factor in the Silver Bridge disaster of 1967 in West Virginia, when a steel suspension bridge collapsed in less than a minute, killing 46 drivers and passengers on the bridge at the time.

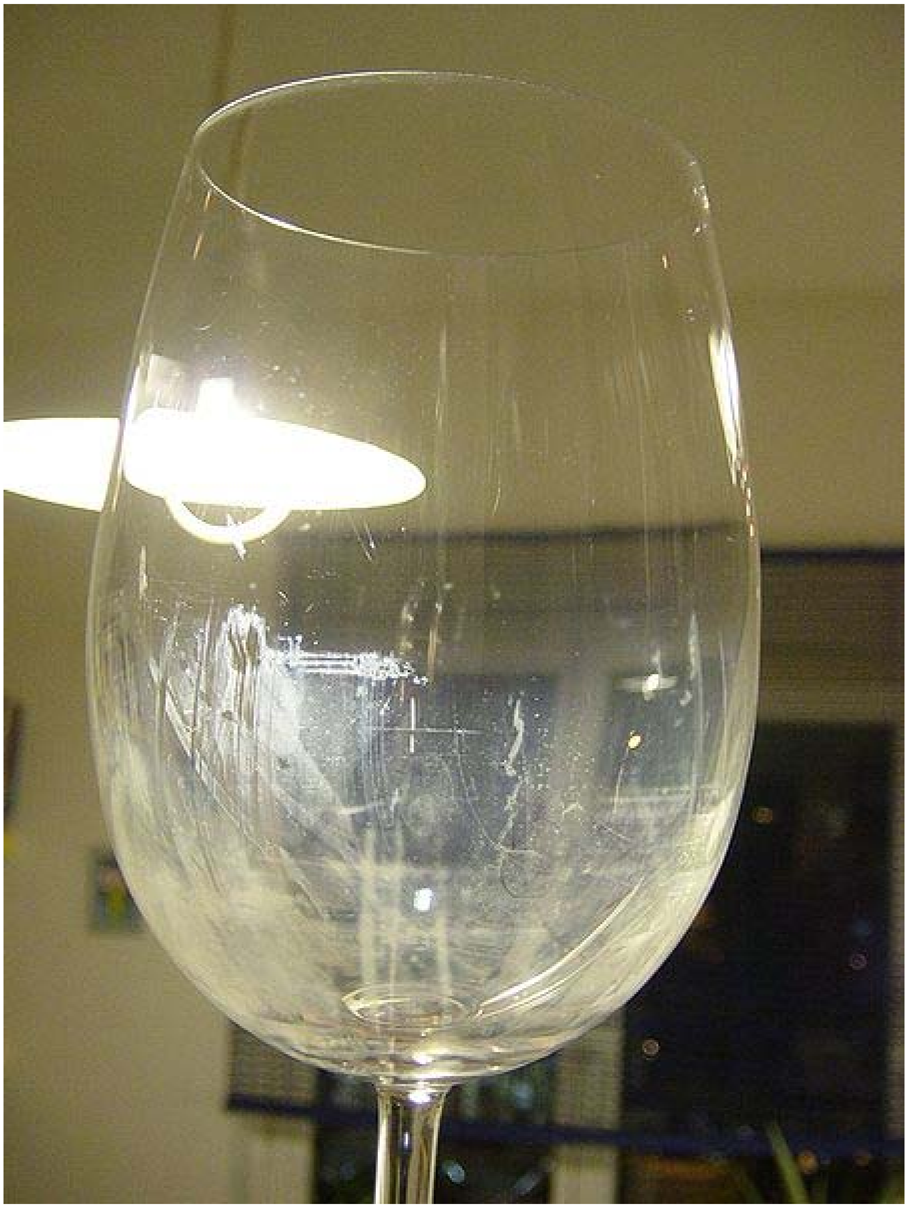
Similarly corrosion of concrete-covered steel and iron can cause the concrete to spall, creating severe structural problems. It is one of the most common failure modes of reinforced concrete bridges. Measuring instruments based on the half-cell potential are able to detect the potential corrosion spots before total failure of the concrete structure is reached.

Corrosion in nonmetals

Most ceramic materials are almost entirely immune to corrosion. The strong ionic and/or covalent bonds that hold them together leave very little free chemical energy in the structure; they can be thought of as already corroded. When corrosion does occur, it is almost always a simple dissolution of the material or chemical reaction, rather than an electrochemical process. A common example of corrosion protection in ceramics is the lime added to soda-lime glass to reduce its solubility in water; though it is not nearly as soluble as pure sodium silicate, normal glass does form sub-microscopic flaws when exposed to moisture. Due to its brittleness, such flaws cause a dramatic reduction in the strength of a glass object during its first few hours at room temperature.

Polymer degradation is due to a wide array of complex and often poorly-understood physiochemical processes. These are strikingly different from the other processes discussed here, and so the term "corrosion" is only applied to them in a loose sense of the word. Because of their large molecular weight, very little entropy can be gained by mixing a given mass of polymer with another substance, making them generally quite difficult to dissolve. While dissolution is a problem in some polymer applications, it is relatively simple to design against. A more common and related problem is *swelling*, where small molecules infiltrate the structure, reducing strength and stiffness and causing a volume change. Conversely, many polymers (notably flexible vinyl) are intentionally swelled with plasticizers, which can be leached out of the structure, causing brittleness or other undesirable changes. The most common form of degradation, however, is a decrease in polymer chain length. Mechanisms which break polymer chains are familiar to biologists because of their effect on DNA: ionizing radiation (most commonly ultraviolet light), free radicals, and oxidizers such as oxygen, ozone, and chlorine. Additives can slow these process very effectively, and can be as simple as a UV-absorbing pigment (i.e., titanium dioxide or carbon black). Plastic shopping bags often do not include these additives so that they break down more easily as litter.

Corrosion of glasses



Glass corrosion

Glass disease is the corrosion of silicate glasses in aqueous solutions. It is governed by two mechanisms: diffusion-controlled leaching (ion exchange) and glass network hydrolytic dissolution. Both corrosion mechanisms strongly depend on the pH of contacting solution: the rate of ion exchange decreases with pH as $10^{-0.5pH}$ whereas the rate of hydrolytic dissolution increases with pH as $10^{0.5pH}$

Mathematically, corrosion rates of glasses are characterised by normalised corrosion rates of elements NR_i (g/cm^2 d) which are determined as the ratio of total amount of released species into the water M_i (g) to the water-contacting surface area S (cm^2), time of contact t (days) and weight fraction content of the element in the glass f_i:

$$NR_i = \frac{M_i}{S f_i t}.$$

The overall corrosion rate is a sum of contributions from both mechanisms (leaching + dissolution) $NR_i = Nrx_i + NRh$. Diffusion-controlled leaching (ion exchange) is characteristic of the initial phase of corrosion and involves replacement of alkali ions in the glass by a hydronium (H_3O^+) ion from the solution. It causes an ion-selective depletion of near surface layers of glasses and gives an inverse square root dependence of corrosion rate with exposure time. The diffusion controlled normalised leaching rate of cations from glasses (g/cm^2 d) is given by:

$$NRx_i = 2\rho\sqrt{\frac{D_i}{\pi t}},$$

where t is time, D_i is the i-th cation effective diffusion coefficient (cm^2/d), which depends on pH of contacting water as $D_i = D_{i0} \cdot 10^{-pH}$, and ρ is the density of the glass (g/cm^3).

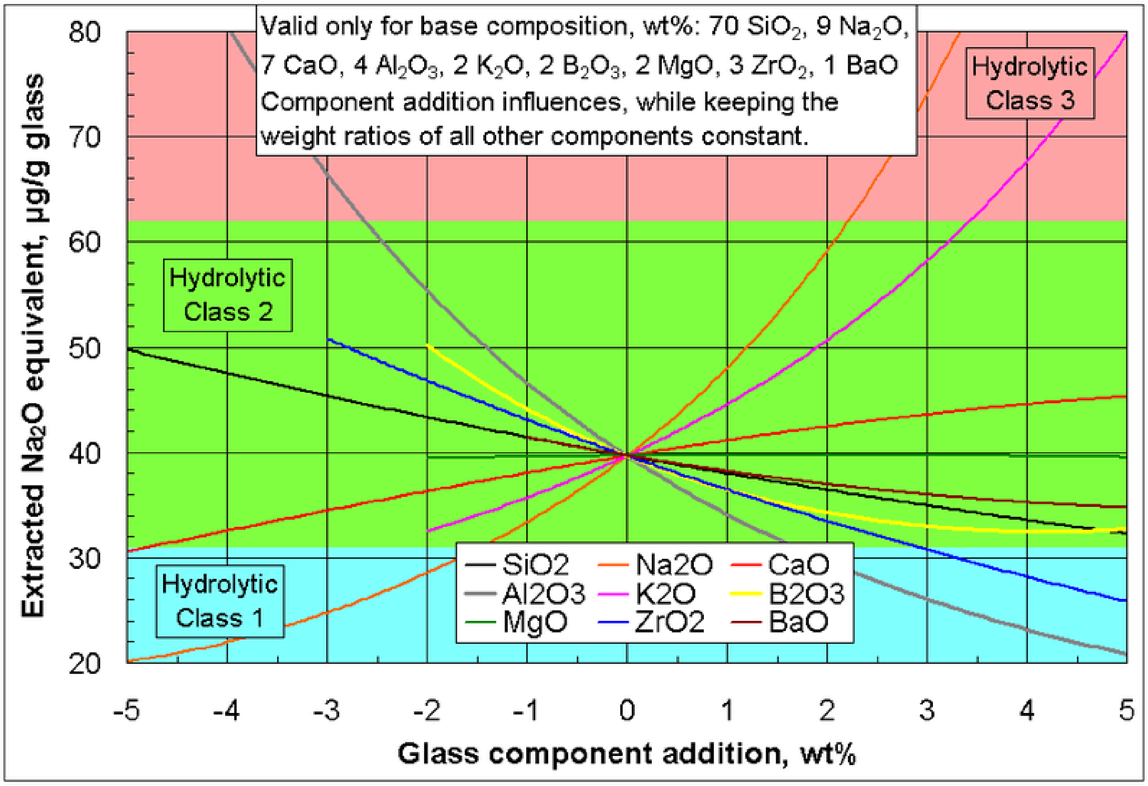
Glass network dissolution is characteristic of the later phases of corrosion and causes a congruent release of ions into the water solution at a time-independent rate in dilute solutions (g/cm^2 d):

$$NRh = \rho r_h,$$

where r_h is the stationary hydrolysis (dissolution) rate of the glass (cm/d). In closed systems the consumption of protons from the aqueous phase increases the pH and causes a fast transition to hydrolysis. However further silica saturation of solution impedes hydrolysis and causes the glass to return to an ion-exchange, e.g. diffusion-controlled regime of corrosion.

In typical natural conditions normalised corrosion rates of silicate glasses are very low and are of the order of 10^{-7} - 10^{-5} g/cm^2 d. The very high durability of silicate glasses in water makes them suitable for hazardous and nuclear waste immobilisation.

Glass corrosion tests



Influences of selected glass component additions on the chemical durability against water corrosion of a specific base glass (corrosion test ISO 719).

There exist numerous standardized procedures for measuring the corrosion (also called **chemical durability**) of glasses in neutral, basic, and acidic environments, under simulated environmental conditions, in simulated body fluid, at high temperature and pressure, and under other conditions.

In the standard procedure ISO 719 a test of the extraction of water soluble basic compounds under neutral conditions is described: 2 g glass, particle size 300-500 µm, is kept for 60 min in 50 ml de-ionized water of grade 2 at 98°C. 25 ml of the obtained solution is titrated against 0.01 mol/l HCl solution. The volume of HCl needed for neutralization is recorded and classified following the values in the table below.

0.01M HCl needed to neutralize extracted basic oxides, ml	**Extracted Na_2O equivalent, µg**	**Hydrolytic class**
to 0.1	to 31	1
above 0.1 to 0.2	above 31 to 62	2
above 0.2 to 0.85	above 62 to 264	3
above 0.85 to 2.0	above 264 to 620	4
above 2.0 to 3.5	above 620 to 1085	5

above 3.5	above 1085	>5

Chapter 2

Ablation

Ablation is removal of material from the surface of an object by vaporization, chipping, or other erosive processes. The term occurs in spaceflight associated with atmospheric reentry, in glaciology, medicine, and passive fire protection.

Ablation near the electrode in a flashtube. The high energy electrical arc slowly erodes the glass, leaving a frosted appearance.

Spaceflight

In spacecraft design, ablation is used to both cool and protect mechanical parts and/or payloads that would otherwise be damaged by extremely high temperatures. Two principal applications are heat shields for spacecraft entering a planetary atmosphere from space and cooling of rocket engine nozzles. Examples include the Apollo Command Module that protected astronauts from the heat of atmospheric reentry and the Kestrel second stage rocket engine designed for exclusive use in an environment of space vacuum since no heat convection is possible.

In a basic sense, ablative material is designed to slowly burn away in a controlled manner, so that heat can be carried away from the spacecraft by the gases generated by the ablative process; while the remaining solid material insulates the craft from superheated gases. There is an entire branch of spaceflight research involving the search for new fireproofing materials to achieve the best ablative performance; this function is critical to protect the spacecraft occupants and payload from otherwise excessive heat loading. The same technology is used in some passive fire protection applications, in some cases by the same vendors, who offer different versions of these fireproofing products, some for aerospace and some for structural fire protection.

Glaciology

In glaciology and meteorology, ablation—the opposite of accumulation—refers to all processes that remove snow, ice, or water from a glacier or snowfield. Ablation refers to the melting of snow or ice that runs off the glacier, evaporation, sublimation, calving, or erosive removal of snow by wind. Air temperature is typically the dominant control of ablation with precipitation exercising secondary control. In a temperate climate during ablation season, ablation rates typically average around 2 mm/hr.

Ablation can refer either to the processes removing ice and snow or to the quantity of ice and snow removed.

Medicine

In medicine, ablation is the same as removal of a part of biological tissue, usually by surgery. Surface ablation of the skin (dermabrasion, also called resurfacing because it induces regeneration) can be carried out by chemicals (which cause peeling) or by lasers. Its purpose is to remove skin spots, aged skin, wrinkles, thus rejuvenating it. Surface ablation is also employed in otolaryngology for several kinds of surgery, such as for snoring. Ablation therapy using radio frequency waves on the heart is used to cure a variety of cardiac arrhythmia such as supraventricular tachycardia, Wolff–Parkinson–White syndrome (WPW), ventricular tachycardia, and more recently as management of atrial fibrillation. The term is often used in the context of laser ablation, a process in which a laser dissolves a material's molecular bonds. For a laser to ablate tissues, the power density or fluence must be high, otherwise thermocoagulation occurs, which is simply thermal vaporization of the tissues.

Rotoablation is a type of arterial cleansing that consists of inserting a tiny, diamond-tipped, drill-like device into the affected artery to remove fatty deposits or plaque. The procedure is used in the treatment of coronary heart disease to restore blood flow.

Radio frequency ablation is a method of removing aberrant tissue from within the body via minimally invasive procedures. i.e.RF ablation in an electrophysiology study to remove cells that are issuing abnormal electrical activity leading to arrhythmia.

Bone marrow ablation is a process whereby the human bone marrow cells are eliminated in preparation for a bone marrow transplant. This is performed using high-intensity chemotherapy and total body irradiation.

Ablation of brain tissue is used for treating certain neurological disorders, particularly Parkinson's disease, and sometimes for psychiatric disorders as well.

Recently, some researchers reported successful results with genetic ablation. In particular, genetic ablation is potentially a much more efficient method of removing unwanted cells, such as tumor cells, because large numbers of animals lacking specific cells could be generated. Genetically ablated lines can be maintained for a prolonged period of time and shared within the research community. Researchers at Columbia University report of reconstituted caspases combined from C. elegans and humans, which maintain a high degree of target specificity. The genetic ablation techniques described could prove useful in battling cancer.

Biology

Ablation in biology can refer to genetic or cell ablation, for example. Genetic ablation describes a gene that has been silenced. It can be used on purpose in experiments where scientists can observe the effect of genetic silencing. Cell ablation is where individual cells are destroyed for experimental reasons.

Laser ablation

An Nd:YAG laser drills a hole through a block of nitrile. The intense burst of infrared radiation ablates the highly absorbing rubber, releasing an eruption of plasma.

Laser ablation is greatly affected by the nature of the material and its ability to absorb energy, therefore the wavelength of the ablation laser should have a minimum absorption depth. While these lasers can average a low power, they can offer peak intensity and fluence given by:

$$\text{Intensity } (\text{W/cm}^2) = \frac{\text{average power (W)}}{\text{focal spot area (cm}^2)}$$
$$\text{Peak intensity } (\text{W/cm}^2) = \frac{\text{peak power (W)}}{\text{focal spot area (cm}^2)}$$
$$\text{Fluence } (\text{J/cm}^2) = \frac{\text{laser pulse energy (J)}}{\text{focal spot area (cm}^2)}$$

while the peak power is

$$\text{Peak power (W)} = \frac{\text{pulse energy (J)}}{\text{pulse duration (s)}}$$

Surface ablation of the cornea for several types of eye refractive surgery is now common, using an excimer laser system (LASIK and LASEK). Since the cornea does not grow back, laser is used to remodel the cornea refractive properties to correct refraction errors, such as astigmatism, myopia, and hyperopia. Laser ablation is also used to remove part of the uterine wall in women with menstruation and adenomyosis problems in a process called endometrial ablation.

Passive fire protection

Firestopping and fireproofing products can be ablative in nature. This can mean endothermic materials, or merely materials that are sacrificial and become "spent" over time while exposed to fire such as silicone firestop products. Given sufficient time under fire or heat conditions, these products char away, crumble, and disappear. The idea is to put enough of this material in the way of the fire that a level of fire-resistance rating can be maintained, as demonstrated in a fire test. Ablative materials usually have a large concentration of organic matter that is reduced by fire to ashes. In the case of silicone, organic rubber surrounds very finely divided silica dust (up to 380 m^2 of combined surface area of all the dust particles per gram of this dust). When the organic rubber is exposed to fire it burns to ash and leaves behind the silica dust with which the product started.

Marine surface coatings

Antifouling paints and other related coatings are routinely used to prevent the buildup of microorganisms and other animals, such as barnacles for the bottom hull surfaces of recreational, commercial and military sea vessels. Ablative paints are often utilized for this purpose to prevent the dilution or deactivation of the antifouling agent. Over time, the paint will slowly decompose in the water, exposing fresh antifouling compounds on the surface. Engineering the antifouling agents and the ablation rate can produce long-lived protection from the deleterious effects of biofouling.

Chapter 3

Chemically Assisted Degradation of Polymers and Coble Creep

Chemically assisted degradation of polymers

Chemically assisted degradation of polymers is a type of polymer degradation that involves a change of the polymer properties due to a chemical reaction with the polymer's surroundings. There are many different types of possible chemical reactions causing degradation however most of these reactions result in the breaking of double bonds within the polymer structure.

Examples of chemically assisted degradation

Degradation of rubber by ozone

One common example of chemically assisted degradation is the degradation of rubber by ozone particles. Ozone is a naturally occurring atmospheric molecule that is produced by electric discharge or through a reaction of Oxygen with solar radiation. Ozone is also produced with atmospheric pollutants reacted with UltraViolet Radiation. For a reaction to occur, ozone concentrations only have to be as low as 3-5 parts per hundred million (pphm) and when these concentrations are reached, a reaction occurs with a thin surface layer (5 x10-7 metres) of the material. The ozone molecules react with the rubber which in most cases is unsaturated (contains double bonds), however a reaction will still occur in saturated polymers (those containing only single bonds). When reaction occurs, scission of the polymer chain (breaking of double covalent bonds) takes place forming decomposition products:

Chain scission increases with the presence of active Hydrogen molecules (for example, in water) as well as acids and alcohols. Along with this type of reaction, cross linking and side branch formations also occur by an activation of the double bond and these make the rubber material more brittle. Due to the increase in brittleness due to the chemical reactions, cracks form in areas of high stress. As propagation of these cracks increases, new surfaces are opened for degradation to occur.

Degradation of poly(vinyl) chloride (PVC)

Degradation can also occur as a result of the formation, and then breakage of double bonds, such as solvolysis in PVC(Peacock). Solvolysis occurs when a Carbon-X bond, with X representing a halogen, is broken. This occurs in PVC in the presence of an acid species. Active Hydrogen atoms will remove a Chlorine atom from the polymer molecule, forming Hydrochloric acid (HCl). The HCl produced may then cause dechlorination of adjacent Carbon atoms. The dechlorinated Carbon atoms then tend to form double bonds, which can be attacked and broken by ozone, just like the degradation of rubbers described above.

Degradation of polyester

Degradation of polyester may occur without the presence of the acidic catalyst that causes degradation of PVC. During hydrolysis water acts as the reactive catalyst instead of the acid. It causes degradation mainly at high temperature and pressure during processing.

In this process the water molecule will attack the C-O ester bond, splitting the polymer in half. The water molecule will then dissociate, with one Hydrogen atom forming a carboxylic acid group on the Carbon atom with the double bonded Oxygen, while the remaining atoms form an alcohol on the other chain end. These reactive products may also cause further degradation of the polymer chain. This chain scission lowers average molecular weight of the polymer, decreasing the number and strength of intermolecular bonds as well as the degree of entanglement. This will increase chain mobility, decreasing strength of the polymer and increasing deformation at low stresses.

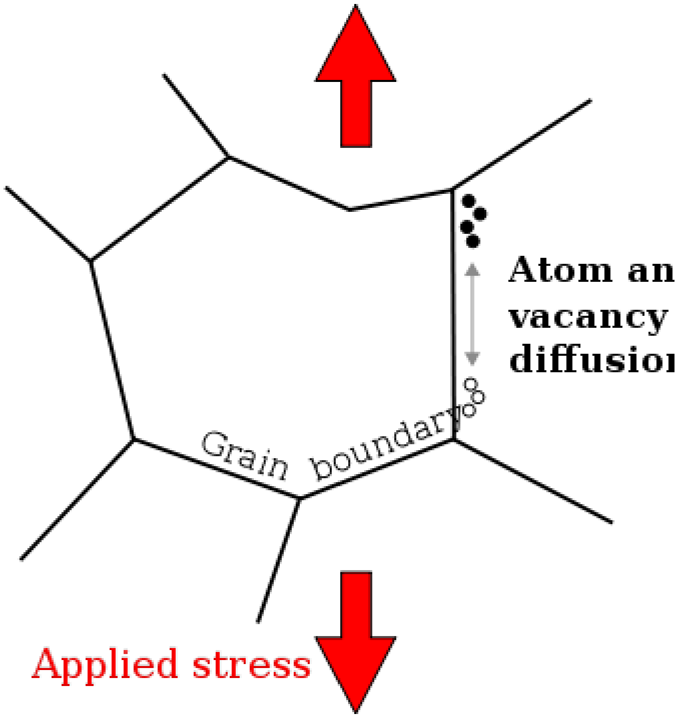
Protection against chemically assisted degradation

Both physical and chemical barriers can be used to protect a polymer from chemically assisted degradation. A physical barrier must provide continuous protection, must not react with the polymer’s environment, must be flexible so that stretching may occur and must also be able to regenerate (after wear processes). A chemical barrier must be highly reactive with the polymer’s surroundings so that the barrier reacts with the environmental conditions rather than the polymer itself. This barrier involves addition of a material into the polymer blend during fabrication of the polymer. Due to this, the barrier addition must have a suitable solubility, must be economically feasible and must not hinder the production process. For the barrier to be activated, the addition must diffuse to the surface and so a suitable diffusivity is also required. There are four theories on how these types of barriers protect the polymer material:

- *Scavenger Theory*: the protective layer reacts with the ozone rather than the polymer.
- *Protective Film Theory*: the protective layer reacts with the polymer producing a thin film on the polymer surface which is inert and cant be penetrated.
- *Re-linking Theory*: the protective layer causes broken double bonds to be reformed.
- *Self Healing Theory*: the protective layer reacts with degraded polymer chains to form low molecular weight material which forms an inert film on the surface.

Of these theories, the Scavenger Theory is the most common and most important. However, more than one theory can act at the same time and the theory that takes place depends on the protective materials, the polymer and surrounding environment.

Coble creep



A diagram showing how atoms and vacancies move through a grain as the mechanism of Coble creep

Coble creep, a form of diffusion creep, is a mechanism for deformation of crystalline solids. Coble creep occurs through the diffusion of atoms in a material along the grain boundaries, which produces a net flow of material and a sliding of the grain boundaries.

Coble creep is named after Robert L. Coble, who first reported his theory of how materials creep over time in 1962 in the Journal of Applied Physics.

The strain rate in a material experiencing Coble creep is given by:

$$\frac{d\epsilon}{dt} = \frac{\sigma}{d^3} D_{gb} e^{-Q_{Coble}/RT}$$

where

- σ is the applied stress
- d is the average grain boundary diameter
- D_{gb} is the diffusion coefficient in the grain boundary
- $-Q_{Coble}$ is the activation energy for Coble creep
- R is the molar gas constant
- T is the temperature in kelvins

Note that in Coble creep, the strain rate $\frac{d\epsilon}{dt}$ is proportional to the applied stress σ; the same relationship is found for Nabarro-Herring creep. However, the two mechanisms differ in their relationship between the strain rate and grain size d. In Coble creep, the strain rate is proportional to d^{-3}, whereas the strain rate in Nabarro-Herring creep is proportional to d^{-2}. Researchers commonly use these relationships to determine which mechanism is dominant in a material; by varying the grain size and measuring how the strain rate is affected, they can

Chapter 4

Corrosion Fatigue

Corrosion fatigue is fatigue in a corrosive environment. It is the mechanical degradation of a material under the joint action of corrosion and cyclic loading. Nearly all engineering structures experience some form of alternating stress and are exposed to harmful environments during their service life. The environment plays a significant role in the fatigue of high strength structural materials like steels, aluminum alloys and titanium alloys. Materials with high specific strength are being developed to meet the requirements of advancing technology. However,their usefulness depends to a large extent on the extent to which they resist corrosion fatigue. Effects of corrosive environments on fatigue behavior of metallic materials have been studied as early as 1930 (1). The phenomenon is not to be confused with stress corrosion cracking, where corrosion such as pitting attack leads to development of brittle cracks, growth and failure. The only requirement is that the sample is under tensile stress.

Effect of corrosion on S-N diagram

Effect of corrosion on smooth specimen S-N diagram is shown schematically in Fig.1. In this figure, curve A shows the fatigue behavior of a material tested in air. A fatigue threshold or limit is seen in A corresponding to the horizontal part of the curve. Curves B and C represent the fatigue behavior of the same material in two corrosive environments. In curve B, the fatigue failure at high stress levels is retarded and the fatigue limit is eliminated. In curve C, the whole curve is shifted to the left indicating a general lowering in the fatigue strength, accelerated initiation at higher stresses and elimination of a fatigue limit. To meet the needs of advancing technology, higher strength materials are developed through heat treatments or alloying. Such higher strength materials generally exhibit higher fatigue limits and thus can be used at higher service stress levels even under fatigue loading. However, presence of corrosive environments during fatigue loading eliminates this stress advantage, as the fatigue limit becomes almost insensitive to the strength level for a particular group of alloys (2). This effect is schematically shown, for the case of several steels, in Fig.2. This figure brings out the debilitating effect of corrosive environments on the functionality of high strength materials under fatigue.

Corrosion fatigue in aqueous media is an electrochemical behavior. Fractures are initiated either by pitting or at persistent slip bands (3). Corrosion fatigue can hence be reduced by alloy additions, inhibition, and cathodic protection all of which reduce pitting (4) Since corrosion fatigue cracks initiate at the metal surface, surface treatments like plating, cladding, nitriding and shot-peening were found to improve the materials' resistance to this phenomenon (5).

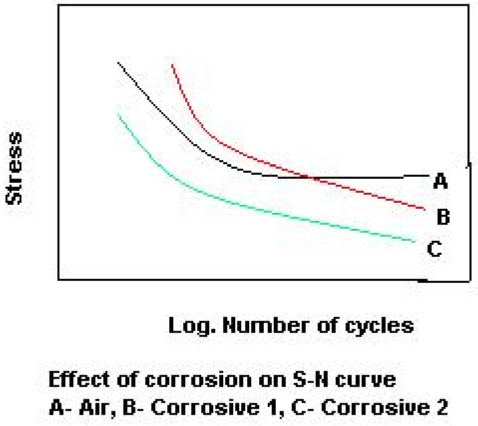


Fig.1 Effect of corrosion on S-N diagram

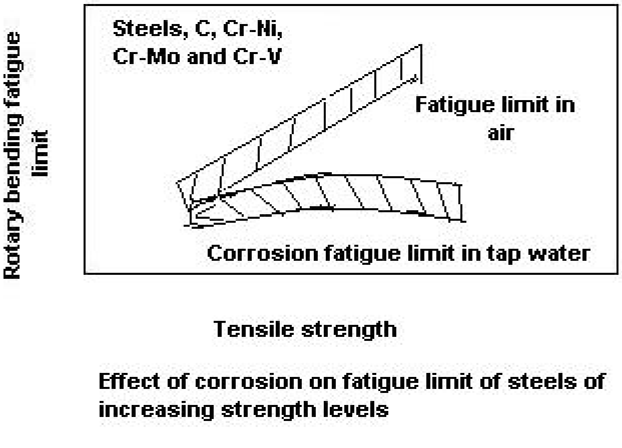


Fig.2 Effect of corrosion on fatigue limits of steels

Crack propagation studies in corrosion fatigue

In normal fatigue testing of smooth specimens, about 90% of the life is spent in crack nucleation and only the remaining 10 % in crack propagation. However,in corrosion fatigue,crack nucleation is facilitated by corrosion and typically about 10 % of life is sufficient for this stage. The rest, 90 % of life is spent in crack propagation. Thus it is much more informative to evaluate the crack propagation behavior during corrosion fatigue. Fracture mechanics uses pre-cracked specimens and effectively measures crack propagation behavior. Hence considerable emphasis is being given to crack propagation velocity measurements using fracture mechanics to study corrosion fatigue. Since fatigue crack grows in a stable fashion below the critical stress intensity factor for fracture (fracture toughness), the process is called sub-critical crack growth. Fig.3 shows a typical fatigue crack growth behavior.

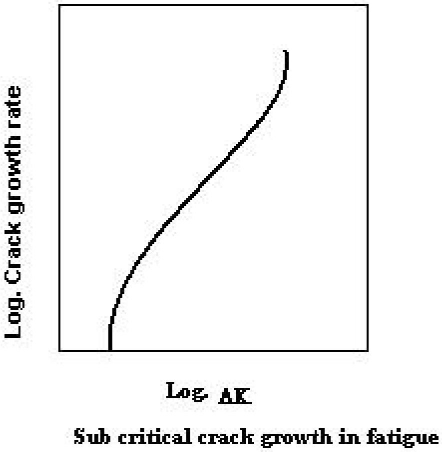


Fig.3. Typical fatigue crack growth behavior(Schematic)

In this log-log plot,the crack propagation velocity is plotted against the applied stress intensity range. Generally there is threshold stress intensity range below which the crack propagation velocity is insignificantly low. Three stages may be visualized in this plot. Near the threshold,crack propagation velocity increases considerably with increasing stress intensity range, a second region where the curve is nearly linear and follows the Paris' law(6), and the third region where crack propagation velocity increases rapidly with stress intensity range leading to fracture at the fracture toughness value.

Crack propagation under corrosion fatigue may be classified in to i) true corrosion fatigue, ii) stress corrosion fatigue and iii) a combination of true, and stress, corrosion fatigues.

True corrosion fatigue

In true corrosion fatigue, the fatigue crack growth rate is enhanced by corrosion and this effect is seen in all the three regions of the fatigue crack growth rate diagram. Fig.4 shows a schematic diagram of crack growth rate under true corrosion fatigue. It is seen from this figure that the whole curve is shifted to lower stress intensity factor range in the corrosive environment. The threshold is lower and the crack growth velocities are higher at all stress intensity factors. The fracture of the specimen occurs when the stress intensity factor range is equal to the applicable threshold stress intensity factor for stress corrosion cracking.

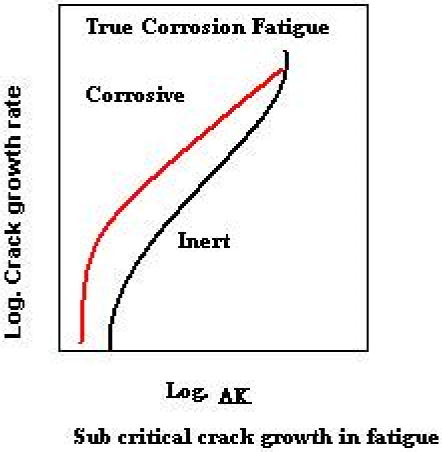


Fig.4 Crack growth behavior under true corrosion fatigue

When attempting to analyze the effects of corrosion fatigue on crack growth in a particular, both corrosion type and fatigue load levels can each affect the crack growth to varying degrees. Common corrosion types include crevice, pitting, filiform, exfoliation, intergranular—each will affect crack growth in a particular material in a distinct way. For instance, pitting corrosion will often be the most damaging type of corrosion, degrading a material's performance (that it, speeds up crack growth rates) more than any of the other kinds of corrosion; even pits the order of a material's grain size can substantially degrade a material. The degree to which corrosion can affect crack growth rates can also be depending on fatigue load levels; for instance, corrosion can cause much greater increase in crack growth rates at low loads than it does at high loads (7).

Stress corrosion fatigue

In materials where the maximum applied stress intensity factor exceeds the stress corrosion cracking threshold value, stress corrosion will also add to the crack growth velocity. This is shown schematically in Fig.5. In the corrosive environment, the crack grows due to cyclic loading at lower stress intensity ranges,but above the threshold stress intensity for scc, additional crack growth (red line) occurs due to stress corrosion cracking. The lower stress intensity regions are not affected and the threshold stress intensity range for fatigue crack propagation is unchanged in the corrosive environment.

In the most general case, corrosion fatigue crack growth may exhibit both of the above effects and the crack growth behavior is represented schematically in Fig.6.

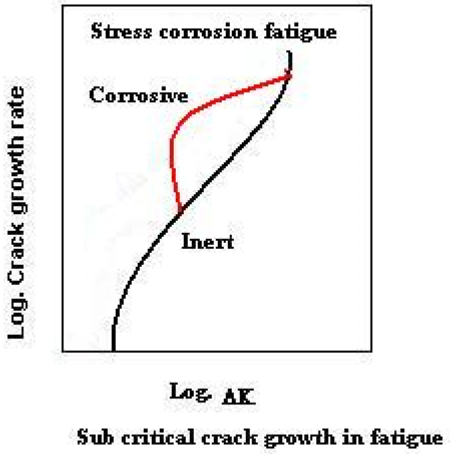


Fig.5 Crack growth behavior under stress corrosion fatigue

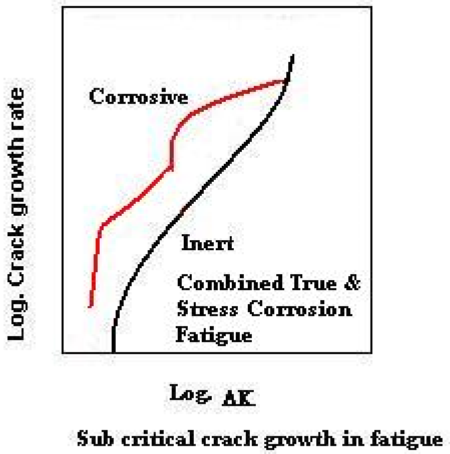


Fig.6. Combined true corrosion fatigue and stress corrosion fatigue.

Chapter 5

Creep (Deformation)

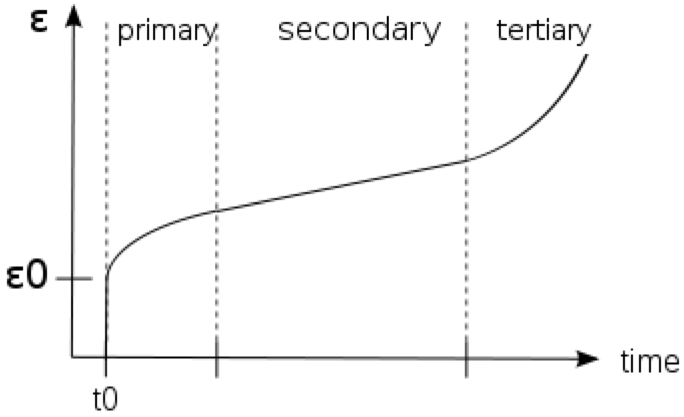
In materials science, **creep** is the tendency of a solid material to slowly move or deform permanently under the influence of stresses. It occurs as a result of long term exposure to high levels of stress that are below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods, and near melting point. Creep always increases with temperature.

The rate of this deformation is a function of the material properties, exposure time, exposure temperature and the applied structural load. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function — for example creep of a turbine blade will cause the blade to contact the casing, resulting in the failure of the blade. Creep is usually of concern to engineers and metallurgists when evaluating components that operate under high stresses or high temperatures. Creep is a deformation mechanism that may or may not constitute a failure mode. Moderate creep in concrete is sometimes welcomed because it relieves tensile stresses that might otherwise lead to cracking.

Unlike brittle fracture, creep deformation does not occur suddenly upon the application of stress. Instead, strain accumulates as a result of long-term stress. Creep is a "time-dependent" deformation.

The temperature range in which creep deformation may occur differs in various materials. For example, tungsten requires a temperature in the thousands of degrees before creep deformation can occur while ice will creep near 0 °C (32 °F). As a rule of thumb, the effects of creep deformation generally become noticeable at approximately 30% of the melting point for metals and 40–50% of melting point for ceramics. Virtually any material will creep upon approaching its melting temperature. Since the minimum temperature is relative to melting point, creep can be seen at relatively low temperatures for some materials. Plastics and low-melting-temperature metals, including many solders, creep at room temperature as can be seen markedly in old lead hot-water pipes. Glacier flow is an example of creep processes in ice.

Stages of creep



Strain as a function of time due to constant stress over an extended period for a viscoelastic material.

In the initial stage, or primary creep, the strain rate is relatively high, but slows with increasing strain. This is due to work hardening. The strain rate eventually reaches a minimum and becomes near constant. This is due to the balance between work hardening and annealing (thermal softening). This stage is known as secondary or steady-state creep. This stage is the most understood. The characterized "creep strain rate" typically refers to the rate in this secondary stage. Stress dependence of this rate depends on the creep mechanism. In tertiary creep, the strain rate exponentially increases with strain because of necking phenomena.

Mechanisms of creep

The mechanism of creep depends on temperature and stress. The various methods are:

- Bulk diffusion (Nabarro-Herring creep)
- Climb — here the strain is actually accomplished by climb
- Climb-assisted glide — here the climb is an *enabling* mechanism, allowing dislocations to get around obstacles
- Grain boundary diffusion (Coble creep)
- Thermally activated glide — e.g., via cross-slip

General creep equation

$$\frac{d\varepsilon}{dt} = \frac{C\sigma^m}{d^b} e^{\frac{-Q}{kT}}$$

where ε is the creep strain, C is a constant dependent on the material and the particular creep mechanism, m and b are exponents dependent on the creep mechanism, Q is the activation energy of the creep mechanism, σ is the applied stress, d is the grain size of the material, k is Boltzmann's constant, and T is the absolute temperature.

Dislocation creep

At high stresses (relative to the shear modulus), creep is controlled by the movement of dislocations. For dislocation creep, $Q = Q(\textit{self diffusion})$, $m = 4\text{-}6$, and $b = 0$. Therefore, dislocation creep has a strong dependence on the applied stress and no grain size dependence.

Some alloys exhibit a very large stress exponent ($n > 10$), and this has typically been explained by introducing a "threshold stress," σ_{th}, below which creep can't be measured. The modified power law equation then becomes:

$$\frac{d\epsilon}{dt} = A\left(\sigma - \sigma_{th}\right)^{n} e^{\frac{-Q}{RT}}$$

where A, Q and n can all be explained by conventional mechanisms (so $3 \leq n \leq 10$).

Nabarro-Herring creep

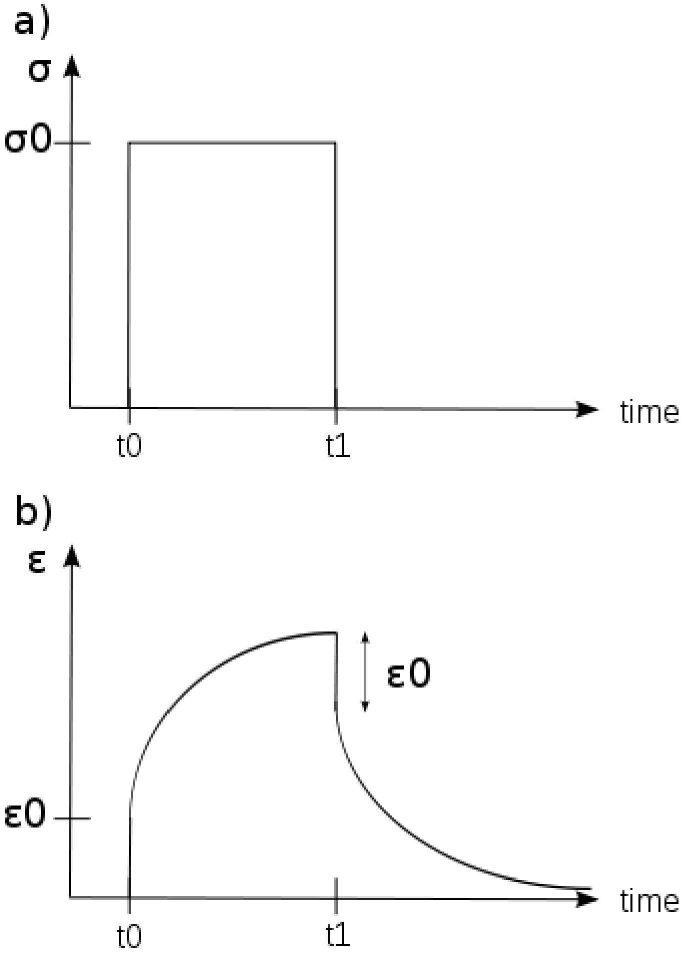
Nabarro-Herring creep is a form of diffusion controlled creep. In Nabarro-Herring creep, atoms diffuse through the lattice causing grains to elongate along the stress axis; k is related to the diffusion coefficient of atoms through the lattice, $Q = Q(\textit{self diffusion})$, $m = 1$, and $b = 2$. Therefore Nabarro-Herring creep has a weak stress dependence and a moderate grain size dependence, with the creep rate decreasing as grain size is increased.

Nabarro-Herring creep is strongly temperature dependent. For lattice diffusion of atoms to occur in a material, neighboring lattice sites or interstitial sites in the crystal structure must be free. A given atom must also overcome the energy barrier to move from its current site (it lies in an energetically favorable potential well) to the nearby vacant site (another potential well). The general form of the diffusion equation is $D = D_0 exp(E/KT)$ where D_0 has a dependence on both the attempted jump frequency and the number of nearest neighbor sites and the probability of the sites being vacant. Thus there is a double dependence upon temperature. At higher temperatures the diffusivity increases due to the direct temperature dependence of the equation, the increase in vacancies through Schottky defect formation, and an increase in the average energy of atoms in the material. Nabarro-Herring creep dominates at very high temperatures relative to a material's melting temperature.

Coble creep

Coble creep is a second form of diffusion controlled creep. In Coble creep the atoms diffuse along grain boundaries to elongate the grains along the stress axis. This causes Coble creep to have a stronger grain size dependence than Nabarro-Herring creep. For Coble creep k is related to the diffusion coefficient of atoms along the grain boundary, $Q = Q(\textit{grain boundary diffusion})$, $m = 1$, and $b = 3$. Because $Q(\textit{grain boundary diffusion}) < Q(\textit{self diffusion})$, Coble creep occurs at lower temperatures than Nabarro-Herring creep. Coble creep is still temperature dependent, as the temperature increases so does the grain boundary diffusion. However, since the number of nearest neighbors is effectively limited along the interface of the grains, and thermal generation of vacancies along the boundaries is less prevalent, the temperature dependence is not as strong as in Nabarro-Herring creep. It also exhibits the same linear dependence on stress as Nabarro-Herring creep.

Creep of polymers



a) Applied stress and b) induced strain as functions of time over a short period for a viscoelastic material.

Creep can occur in polymers and metals which are considered viscoelastic materials. When a polymeric material is subjected to an abrupt force, the response can be modeled using the Kelvin-Voigt model. In this model, the material is represented by a Hookean spring and a Newtonian dashpot in parallel. The creep strain is given by

$$\varepsilon(t) = \sigma C_0 + \sigma C \int_0^\infty f(\tau)(1 - \exp[-t/\tau])\, d\tau$$

where:

- σ = applied stress
- C_0 = *instantaneous creep compliance*
- C = creep compliance coefficient
- τ = retardation time
- $f(\tau)$ = distribution of retardation times

When subjected to a step constant stress, viscoelastic materials experience a time-dependent increase in strain. This phenomenon is known as viscoelastic creep.

At a time t_0, a viscoelastic material is loaded with a constant stress that is maintained for a sufficiently long time period. The material responds to the stress with a strain that increases until the material ultimately fails. When the stress is maintained for a shorter time period, the material undergoes an initial strain until a time t_1 at which the stress is relieved, at which time the strain immediately decreases (discontinuity) then continues decreasing gradually to a residual strain.

Viscoelastic creep data can be presented in one of two ways. Total strain can be plotted as a function of time for a given temperature or temperatures. Below a critical value of applied stress, a material may exhibit linear viscoelasticity. Above this critical stress, the creep rate grows disproportionately faster. The second way of graphically presenting viscoelastic creep in a material is by plotting the creep modulus (constant applied stress divided by total strain at a particular time) as a function of time. Below its critical stress, the viscoelastic creep modulus is independent of stress applied. A family of curves describing strain versus time response to various applied stress may be represented by a single viscoelastic creep modulus versus time curve if the applied stresses are below the material's critical stress value.

Additionally, the molecular weight of the polymer of interest is known to affect its creep behavior. The effect of increasing molecular weight tends to promote secondary bonding between polymer chains and thus make the polymer more creep resistant. Similarly, aromatic polymers are even more creep resistant due to the added stiffness from the rings. Both molecular weight and aromatic rings add to polymers' thermal stability, increasing the creep resistance of a polymer.

Both polymers and metals can creep. Polymers experience significant creep at temperatures above ca. –200°C; however, there are three main differences between polymeric and metallic creep.

Polymers show creep basically in two different ways. At typical work loads (5 up to 50%) ultra high molecular weight polyethylene (Spectra, Dyneema) will show time-linear creep, whereas polyester or aramids (Twaron, Kevlar) will show a time-logarithmic creep.

Applications

Though mostly due to the reduced yield stress at higher temperatures, the Collapse of the World Trade Center was due in part to creep from increased temperature operation.

The creep rate of hot pressure-loaded components in a nuclear reactor at power can be a significant design-constraint, since the creep rate is enhanced by the flux of energetic particles.

Creep was blamed for the Big Dig tunnel ceiling collapse in Boston, Massachusetts that occurred in July 2006.

An example of an application involving creep deformation is the design of tungsten light bulb filaments. Sagging of the filament coil between its supports increases with time due to creep deformation caused by the weight of the filament itself. If too much deformation occurs, the adjacent turns of the coil touch one another, causing an electrical short and local overheating, which quickly leads to failure of the filament. The coil geometry and supports are therefore designed to limit the stresses caused by the weight of the filament, and a special tungsten alloy with small amounts of oxygen trapped in the crystallite grain boundaries is used to slow the rate of Coble creep.

In steam turbine power plants, pipes carry steam at high temperatures (566 °C or 1050 °F) and pressures (above 24.1 MPa or 3500 psi). In jet engines, temperatures can reach up to 1400 °C (2550 °F) and initiate creep deformation in even advanced-coated turbine blades. Hence, it is crucial for correct functionality to understand the creep deformation behavior of materials.

Creep deformation is important not only in systems where high temperatures are endured such as nuclear power plants, jet engines and heat exchangers, but also in the design of many everyday objects. For example, metal paper clips are stronger than plastic ones because plastics creep at room temperatures. Aging glass windows are often erroneously used as an example of this phenomenon: measurable creep would only occur at temperatures above the glass transition temperature around 500 °C (900 °F). While glass does exhibit creep under the right conditions, apparent sagging in old windows may instead be a consequence of obsolete manufacturing processes, such as that used to create crown glass, which resulted in inconsistent thickness.

Chapter 6

Factors of Polymer Weathering

The **aging of natural and artificial polymeric materials** is a natural phenomenon in (metals, glass, minerals and other inorganic materials. The main environmental parameters influencing the degradation of polymeric materials is daylight combined with the effects of temperature, moisture and oxygen. These act as the main parameters of stress for outdoor weathering.

Introduction

The components of the weather cycles responsible for the deterioration of most materials are non-ionizing radiation, atmospheric temperature and moisture in its various forms. This, combined with the effects of wind and atmospheric gases and pollutants. Although the ultraviolet (UV) portion of solar radiation is mainly responsible for initiating weathering effects, the visible and near-infrared portions can also contribute to the weathering processes. Colored materials are susceptible to visible radiation, and near-infrared radiation can accelerate chemical reactions by raising the material temperature. The other factors act synergistically with solar radiation to significantly influence the weathering processes. All weather factors, including the quality and quantity of sunlight, vary with geographic location, time of day and year, and climatalogical conditions. In order to fully understand and predict the effect of weather on materials, data is required on each factor that may contribute to degradation.

Solar Radiation

Physical changes resulting from exposure to the environment are initiated by chemical bond breaking reactions caused by the absorbed light, either through direct or indirect processes. Chemical bond breaking is a prerequisite to any chemical reaction, and chemical reactions are a prerequisite to observable or measurable physical changes. Other weather factors mainly promote weathering through their influence on the secondary reactions which follow the breaking of bonds. Degradation of most materials exposed to outdoor conditions is caused mainly by the ultraviolet portion of solar energy, with the shortest wavelengths often having the greatest effect. Therefore, variations in both the quantity and quality of ultraviolet in both the direct solar beam and diffuse sky radiation are important factors in the design and evaluation of weathering tests.

Temperature

The temperature of materials exposed to solar radiation has a significant influence on the effect of the radiation. The destructive effects of light are usually accelerated at elevated temperatures as a result of the increased rate of secondary reactions, with reaction rates about doubling with each 10°C rise; this may not be true of all materials but is often found with polymers. At high temperatures molecules have greater mobility. Therefore, the rate of oxygen diffusion increases and free radical fragments formed in primary photochemical processes are more readily separated. Thus, the chance of recombination is reduced and secondary reactions are promoted. Reactions may take place at higher temperatures that occur at a very low rate or not at all at lower temperatures.

In the presence of sunlight the surface temperature of an object is usually considerably higher than the temperature of the air. Solar absorptivity is closely related to color, varying from about 20% for white materials to 90% for black materials; thus samples of different colors will reach different on-exposure temperatures. Because the thermal conductivity and heat capacity of polymeric materials are generally low, much higher temperatures can be obtained on the surface than in the bulk of the material. Therefore, both the surface temperatures of the samples, produced largely by infrared radiation absorption which varies by material color, and ambient air temperature and its fluctuations during exposure do play a role.

Diurnal and seasonal variations occur in solar radiation. Temperature cycling can cause mechanical stress, particularly in composite systems consisting of materials with widely differing temperature coefficients of expansion. Temperature and its cycles are also closely linked with water in all of its forms. Drops in temperature can cause water to condense on the material as dew, a rise in temperature causes evaporation, and sudden rainfall can cause thermal stress.

Moisture

Moisture can take the form of humidity, dew, rain, snow, frost or hail, depending on the ambient temperature. Moisture, in combination with solar radiation, contributes significantly to the weathering of many materials. This is due both to the mechanical stresses imposed when moisture is absorbed or desorbed and to the chemical participation of moisture in the chemical evolution (and in some instances physical effects such as impact). The span of time over which the precipitation occurs and the frequency of wetness are more important in the weathering of materials than the total amount of precipitation. The mechanical stresses induced by freeze/thaw cycling can cause structural failures in some systems, or accelerate degradation already initiated.

Moisture participates both physically and chemically in degradation. Water absorption by synthetic materials and coatings from humidity and direct wetness is a diffusion controlled process. This hydration of the surface layers produces a volume expansion which places mechanical stress on the dry subsurface layers. A following drying out period signifies a desorption of water. The drying out of the surface layers would lead to a volume contraction; the hydrated inner layers resist this contraction, leading to surface stress cracking. This oscillation between hydrated and dehydrated states may result in stress fractures. Because of diffusion rates in organic materials, it may takes weeks or months to reach a moisture equilibrium.

The chemical effects of moisture can be seen in the chalking of titanium dioxide (TiO2) pigmented coatings and polymers; the anatase form is particularly sensitive to wavelengths below about 405 nm while the rutile forms absorb energy above that wavelength. Chalking results from the degradation of the binding material resulting in a release of the TiO2 pigment particles. These particles form a dull layer on the surface which may be wiped off. Experience shows that chalking is strongest where more water is available on the surface; little to no chalking occurs in dry atmospheres. TiO2 is a semiconductor where electron transitions from the valence band to the conduction band result from the absorption of light at wavelengths in the near UV range, below 400 nm. Ultraviolet radiation causes electron hole pairs to be created in the TiO2 lattice. These react with the hydroxide groups on the surface and the Ti4+ ions. Hydroxyl and perhydroxyl radicals are formed through the conversion of oxygen and a water molecule whereby the TiO2 surface again resumes the initial form and acts as a catalyst for continued activity, thus repeating the chalking cycle. The hydroxide and perhydroxyl radical then cause oxidative decomposition of the binder with the subsequent release of TiO2 particles.

Atmospheric Oxygen

Photooxidation accounts for most polymer failures that occur during outdoor exposure. It results from the effects of solar radiation in combination with oxygen. Oxygen can promote degradation in several ways. Free radicals, formed as a result of the cleavage of chemical bonds by solar radiation, react with oxygen to form peroxy radicals that initiate a series of radical chain reactions. The destructive effect of the radiation is multiplied manifold by propagation of bond breakage and the formation of hydroperoxides that further absorb solar ultraviolet radiation. This cascade effect results in an auto-acceleration of the weathering process, and may partially account for the general non-linearity of the weathering response to radiant exposure.

In addition to the reactions of oxygen in its normal ground state, some reactions of oxygen are due to the excited singlet state, a highly reactive form of the molecule. Singlet oxygen is responsible for the rapid deterioration of materials, particularly those with conjugated unsaturation such as natural rubber and synthetic elastomers. It is formed when triplet oxygen, the normal ground state, reacts with sensitizers, such as certain dyes and ketones, excited by radiation to their triplet states. Oxygen also increases the amount of solar radiation absorbed by conjugated unsaturated hydrocarbons through formation of a complex with these materials.

The extent of photochemical reactions involving oxygen differ in the inner and outer layers of both aromatic and aliphatic polymers due to their dependence on the diffusion of oxygen through the polymer. Photooxidation is significantly reduced at depths beyond which oxygen penetrates. Studies of the degradation profiles of low density polyethylene (LDPE), polymethylmethacrylate (PMMA) and polyvinylchloride (PVC) show that photooxidation was higher at the front and back surfaces than in the interior bulk of the material. Because ultraviolet radiation is not strongly absorbed by these materials, a considerable amount of the radiation incident on the front surface is transmitted to the back surface where it initiates photooxidation.

Secondary factors of weather

Ozone is produced by short wavelength (110 nm - 220 nm) UV photolysis of oxygen in the upper atmosphere. The photochemical reaction of nitrogen oxides and hydrocarbons from automobile exhausts is another source. Ozone plays a dual role in weathering. The concentrated layer in the upper atmosphere absorbs the short wavelength ($\leq$300 nm) ultraviolet radiation emitted by the sun and thus plays a critical role in protecting terrestrial objects from this actinic radiation. Ozone is also a powerful oxidant and reported to react rapidly with elastomers and other unsaturated polymers. Ozonolysis typically results in stiffening and cracking, particularly under mechanical stress. However, the contribution of ozonolysis reactions to the overall photooxidation process is still subject to controversy.

Atmospheric pollutants (e.g., sulfur dioxide, nitrogen oxides, hydrocarbons, etc.), in combination with solar radiation, can also be responsible for severe damage. Acid-base induced chemical changes may also be responsible for much pollution-caused damage. Unsaturated alkyl and aromatic compounds may act as catalysts in the photooxidation of polymers. In the presence of sulfur dioxide and oxygen, ultraviolet radiation causes crosslinking of polyethylene and polypropylene and is responsible for the rapid loss of color in pigmented coatings.

Moisture, in combination with temperature, may also promote microbial growth. Mold, mildew and other microbiological and botanical agents may play a significant role in material degradation, particularly in tropical and subtropical climates, although they may not be generally thought of as weathering factors.

Chapter 7

Fatigue (Material)

In materials science, **fatigue** is the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. The nominal maximum stress values are less than the ultimate tensile stress limit, and may be below the yield stress limit of the material.

Fatigue occurs when a material is subjected to repeated loading and unloading. If the loads are above a certain threshold, microscopic cracks will begin to form at the surface. Eventually a crack will reach a critical size, and the structure will suddenly fracture. The shape of the structure will significantly affect the fatigue life; square holes or sharp corners will lead to elevated local stresses where fatigue cracks can initiate. Round holes and smooth transitions or fillets are therefore important to increase the fatigue strength of the structure.

Fatigue life

ASTM defines *fatigue life*, N_f, as the number of stress cycles of a specified character that a specimen sustains before failure of a specified nature occurs.

One method to predict fatigue life of materials is the Uniform Material Law (UML). UML was developed for fatigue life prediction of aluminum and titanium alloys by the end of 20th century and extended to high-strength steels.

Characteristics of fatigue

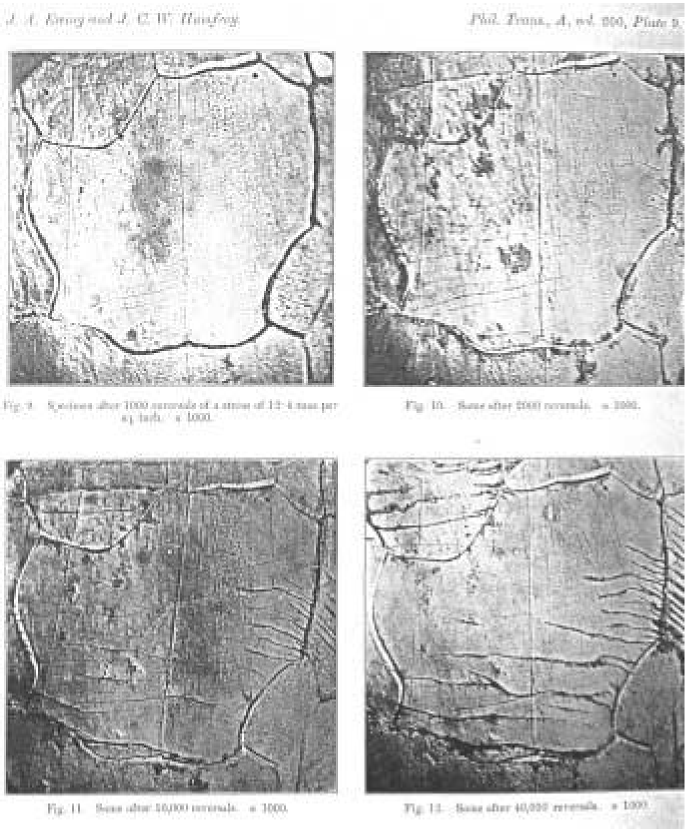
Fracture of an aluminium crank arm. Dark area of striations: slow crack growth. Bright granular area: sudden fracture.

- In metals and alloys, the process starts with dislocation movements, eventually forming persistent slip bands that nucleate short cracks.
- Fatigue is a stochastic process, often showing considerable scatter even in controlled environments.
- The greater the applied stress range, the shorter the life.
- Fatigue life scatter tends to increase for longer fatigue lives.
- Damage is cumulative. Materials do not recover when rested.
- Fatigue life is influenced by a variety of factors, such as temperature, surface finish, microstructure, presence of oxidizing or inert chemicals, residual stresses, contact (fretting), etc.
- Some materials (e.g., some steel and titanium alloys) exhibit a theoretical fatigue limit below which continued loading does not lead to structural failure.

- In recent years, researchers (see, for example, the work of Bathias, Murakami, and Stanzl-Tschegg) have found that failures occur below the theoretical fatigue limit at very high fatigue lives (10^9 to 10^{10} cycles). An ultrasonic resonance technique is used in these experiments with frequencies around 10–20 kHz.
- High cycle fatigue strength (about 10^3 to 10^8 cycles) can be described by stress-based parameters. A load-controlled servo-hydraulic test rig is commonly used in these tests, with frequencies of around 20–50 Hz. Other sorts of machines—like resonant magnetic machines—can also be used, achieving frequencies up to 250 Hz.
- Low cycle fatigue (typically less than 10^3 cycles) is associated with widespread plasticity in metals; thus, a strain-based parameter should be used for fatigue life prediction in metals and alloys. Testing is conducted with constant strain amplitudes typically at 0.01–5 Hz.

Timeline of early fatigue research history

- 1837: Wilhelm Albert publishes the first article on fatigue. He devised a test machine for conveyor chains used in the Clausthal mines.
- 1839: Jean-Victor Poncelet describes metals as being *tired* in his lectures at the military school at Metz.
- 1842: William John Macquorn Rankine recognises the importance of stress concentrations in his investigation of railroad axle failures. The Versailles train crash was caused by axle fatigue.
- 1843: Joseph Glynn reports on fatigue of axle on locomotive tender. He identifies the keyway as the crack origin.
- 1848: Railway Inspectorate report one of the first tyre failures, probably from a rivet hole in tread of railway carriage wheel. It was likely a fatigue failure.
- 1849: Eaton Hodgkinson is granted a *small sum of money* to report to the UK Parliament on his work in *ascertaining by direct experiment, the effects of continued changes of load upon iron structures and to what extent they could be loaded without danger to their ultimate security*.
- 1854: Braithwaite reports on common service fatigue failures and coins the term *fatigue*.
- 1860: Systematic fatigue testing undertaken by Sir William Fairbairn and August Wöhler.
- 1870: Wöhler summarises his work on railroad axles. He concludes that cyclic stress range is more important than peak stress and introduces the concept of *endurance limit*.



J. A. Ewing and J. C. W. Humfrey.

Phil. Trans., A, vol. 200, Plate 9.

Fig. 9. Specimen after 1000 reversals of a stress of 12·4 tons per sq. inch. × 1000.

Fig. 10. Same after 2000 reversals. × 1000.

Fig. 11. Same after 10,000 reversals. × 1000.

Fig. 12. Same after 40,000 reversals. × 1000.

Micrographs showing how surface fatigue cracks grow as material is further cycled. From Ewing & Humfrey (1903)

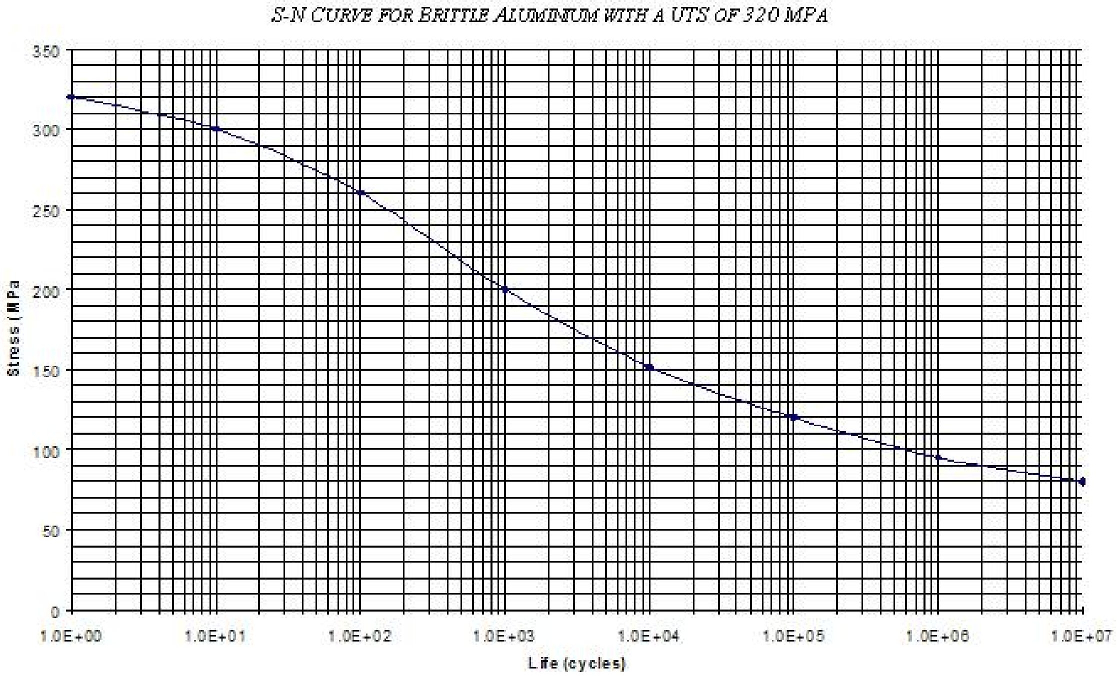
- 1903: Sir James Alfred Ewing demonstrates the origin of fatigue failure in microscopic cracks.
- 1910: O. H. Basquin proposes a log-log relationship for SN curves, using Wöhler's test data.
- 1945: A. M. Miner popularises A. Palmgren's (1924) linear damage hypothesis as a practical design tool.
- 1954: L. F. Coffin and S. S. Manson explain fatigue crack-growth in terms of plastic strain in the tip of cracks.
- 1961: P. C. Paris proposes methods for predicting the rate of growth of individual fatigue cracks in the face of initial scepticism and popular defence of Miner's phenomenological approach.
- 1968: Tatsuo Endo and M. Matsuishi devise the rainflow-counting algorithm and enable the reliable application of Miner's rule to random loadings.
- 1970: W. Elber elucidates the mechanisms and importance of crack closure in slowing the growth of a fatigue crack due to the wedging effect of plastic deformation left behind the tip of the crack.

High-cycle fatigue

Historically, most attention has focused on situations that require more than 10^4 cycles to failure where stress is low and deformation primarily elastic.

The S-N curve

In high-cycle fatigue situations, materials performance is commonly characterised by an *S-N curve*, also known as a *Wöhler curve* . This is a graph of the magnitude of a cyclic stress (*S*) against the logarithmic scale of cycles to failure (*N*).

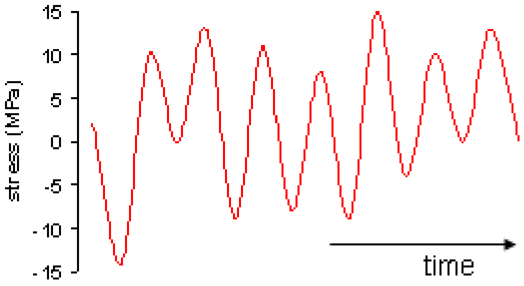


S-N curves are derived from tests on samples of the material to be characterised (often called *coupons*) where a regular sinusoidal stress is applied by a testing machine which also counts the number of cycles to failure. This process is sometimes known as *coupon testing*. Each coupon test generates a point on the plot though in some cases there is a *runout* where the time to failure exceeds that available for the test. Analysis of fatigue data requires techniques from statistics, especially survival analysis and linear regression.

Probabilistic nature of fatigue

As coupons sampled from a homogeneous frame will manifest variation in their number of cycles to failure, the S-N curve should more properly be an *S-N-P curve* capturing the probability of failure after a given number of cycles of a certain stress. Probability distributions that are common in data analysis and in design against fatigue include the lognormal distribution, extreme value distribution, Birnbaum–Saunders distribution, and Weibull distribution.

Complex loadings



Spectrum loading

In practice, a mechanical part is exposed to a complex, often random, sequence of loads, large and small. In order to assess the safe life of such a part:

1. Reduce the complex loading to a series of simple cyclic loadings using a technique such as rainflow analysis;
2. Create a histogram of cyclic stress from the rainflow analysis to form a fatigue damage spectrum;
3. For each stress level, calculate the degree of cumulative damage incurred from the S-N curve; and
4. Combine the individual contributions using an algorithm such as *Miner's rule*.

Miner's rule

In 1945, M. A. Miner popularised a rule that had first been proposed by A. Palmgren in 1924. The rule, variously called *Miner's rule* or the *Palmgren-Miner linear damage hypothesis*, states that where there are k different stress magnitudes in a spectrum, S_i $(1 \le i \le k)$, each contributing $n_i(S_i)$ cycles, then if $N_i(S_i)$ is the number of cycles to failure of a constant stress reversal S_i, failure occurs when:

$$\sum_{i=1}^{k} \frac{n_i}{N_i} = C$$

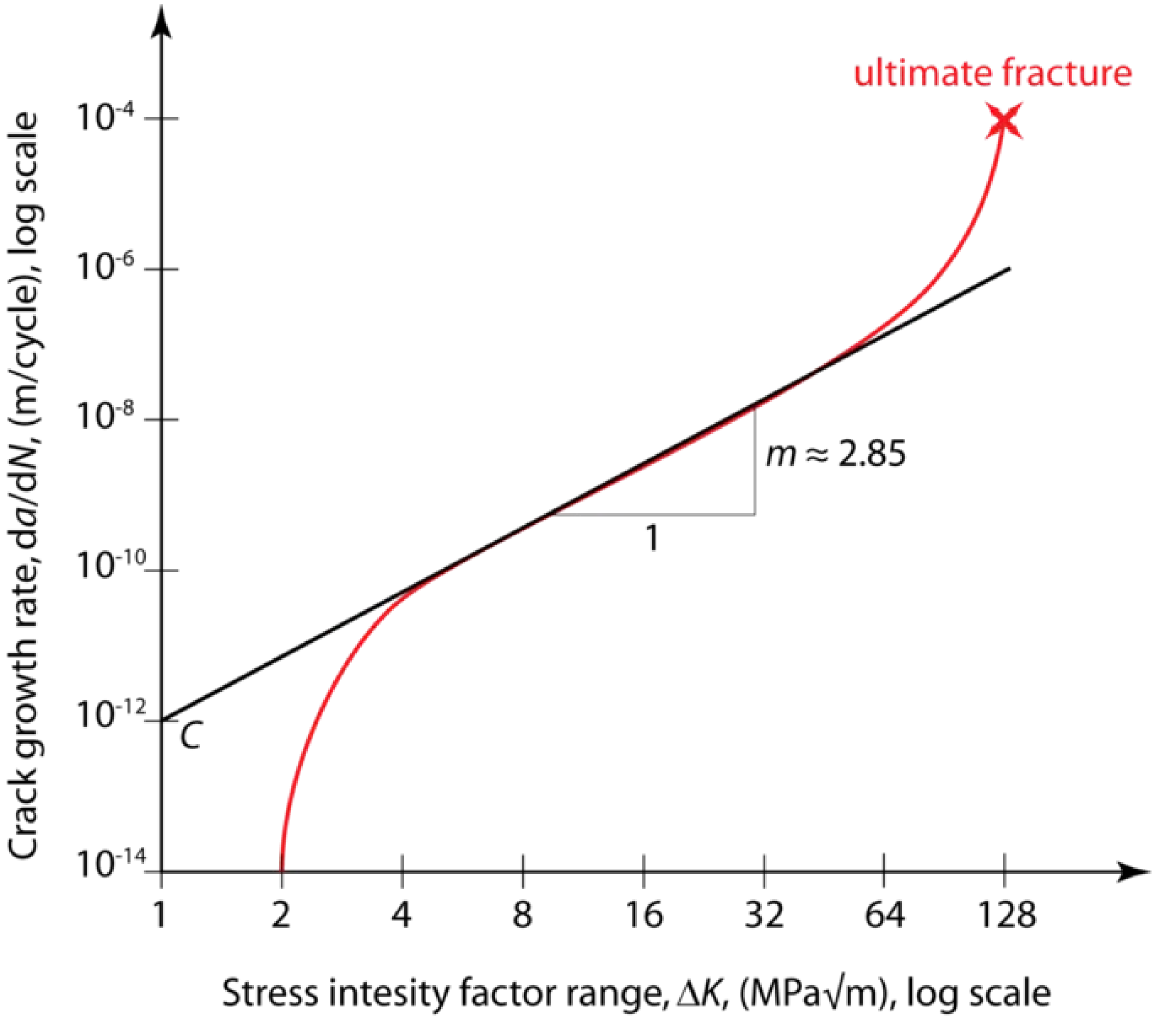
C is experimentally found to be between 0.7 and 2.2. Usually for design purposes, C is assumed to be 1.

This can be thought of as assessing what proportion of life is consumed by stress reversal at each magnitude then forming a linear combination of their aggregate.

Though Miner's rule is a useful approximation in many circumstances, it has several major limitations:

1. It fails to recognise the probabilistic nature of fatigue and there is no simple way to relate life predicted by the rule with the characteristics of a probability distribution. Industry analysts often use design curves, adjusted to account for scatter, to calculate $N_i(S_i)$.
2. There is sometimes an effect in the order in which the reversals occur. In some circumstances, cycles of low stress followed by high stress cause more damage than would be predicted by the rule. It does not consider the effect of overload or high stress which may result in a compressive residual stress. High stress followed by low stress may have less damage due to the presence of compressive residual stress.

Paris' Relationship



Typical fatigue crack growth rate graph.

In Fracture mechanics, Anderson, Gomez and Paris derived relationships for the stage II crack growth with cycles N, in terms of the cyclical component ΔK of the Stress Intensity Factor K

$$\frac{\mathrm{d}a}{\mathrm{d}N} = C(\Delta K)^m$$

where a is the crack length and m is typically in the range 3 to 5 (for metals).

This relationship was later modified (by Forman, 1967) to make better allowance for the mean stress, by introducing a factor depending on (1-R) where R = min stress/max stress, in the denominator.

Low-cycle fatigue

Where the stress is high enough for plastic deformation to occur, the account in terms of stress is less useful and the strain in the material offers a simpler description. Low-cycle fatigue is usually characterised by the *Coffin-Manson relation* (published independently by L. F. Coffin in 1954 and S. S. Manson 1953):

$$\frac{\Delta\epsilon_p}{2} = \epsilon_f'(2N)^c$$

-where:

- $\Delta\varepsilon_p$ /2 is the plastic strain amplitude;
- ε_f' is an empirical constant known as the *fatigue ductility coefficient*, the failure strain for a single reversal;
- 2*N* is the number of reversals to failure (*N* cycles);
- *c* is an empirical constant known as the *fatigue ductility exponent*, commonly ranging from -0.5 to -0.7 for metals in time independent fatigue. Slopes can be considerably steeper in the presence of creep or environmental interactions.

A similar relationship for materials such as Zirconium, used in the nuclear industry.

Fatigue and fracture mechanics

The account above is purely empirical and, though it allows life prediction and design assurance, life improvement or design optimisation can be enhanced using fracture mechanics. It can be developed in four stages.

1. Crack nucleation;
2. Stage I crack-growth;
3. Stage II crack-growth; and
4. Ultimate ductile failure.

Factors that affect fatigue-life

- **Cyclic stress state:** Depending on the complexity of the geometry and the loading, one or more properties of the stress state need to be considered, such as stress amplitude, mean stress, biaxiality, in-phase or out-of-phase shear stress, and load sequence,
- **Geometry:** Notches and variation in cross section throughout a part lead to stress concentrations where fatigue cracks initiate.
- **Surface quality.** Surface roughness cause microscopic stress concentrations that lower the fatigue strength. Compressive residual stresses can be introduced in the surface by e.g. shot peening to increase fatigue life. Such techniques for producing surface stress are often referred to as *peening*, whatever the mechanism used to produce the stress. Low Plasticity Burnishing, Laser peening, and ultrasonic impact treatment can also produce this surface compressive stress and can increase the fatigue life of the component. This improvement is normally observed only for high-cycle fatigue.

- **Material Type:** Fatigue life, as well as the behavior during cyclic loading, varies widely for different materials, e.g. composites and polymers differ markedly from metals.

- **Residual stresses:** Welding, cutting, casting, and other manufacturing processes involving heat or deformation can produce high levels of tensile residual stress, which decreases the fatigue strength.

- **Size and distribution of internal defects:** Casting defects such as gas porosity, non-metallic inclusions and shrinkage voids can significantly reduce fatigue strength.

- **Direction of loading:** For non-isotropic materials, fatigue strength depends on the **direction of the principal stress**.

- **Grain size:** For most metals, smaller grains yield longer fatigue lives, however, the presence of surface defects or scratches will have a greater influence than in a coarse grained alloy.

- **Environment:** Environmental conditions can cause erosion, corrosion, or gas-phase embrittlement, which all affect fatigue life. Corrosion fatigue is a problem encountered in many aggressive environments.

- **Temperature:** Extreme high or low temperatures can decrease fatigue strength.

Design against fatigue

Dependable design against fatigue-failure requires thorough education and supervised experience in structural engineering, mechanical engineering, or materials science. There are three principal approaches to life assurance for mechanical parts that display increasing degrees of sophistication:

1. Design to keep stress below threshold of fatigue limit (infinite lifetime concept);
2. Design (conservatively) for a fixed life after which the user is instructed to replace the part with a new one (a so-called *lifed* part, finite lifetime concept, or "safe-life" design practice);
3. Instruct the user to inspect the part periodically for cracks and to replace the part once a crack exceeds a critical length. This approach usually uses the technologies of nondestructive testing and requires an accurate prediction of the rate of crack-growth between inspections. This is often referred to as damage tolerant design or "retirement-for-cause".

Stopping fatigue

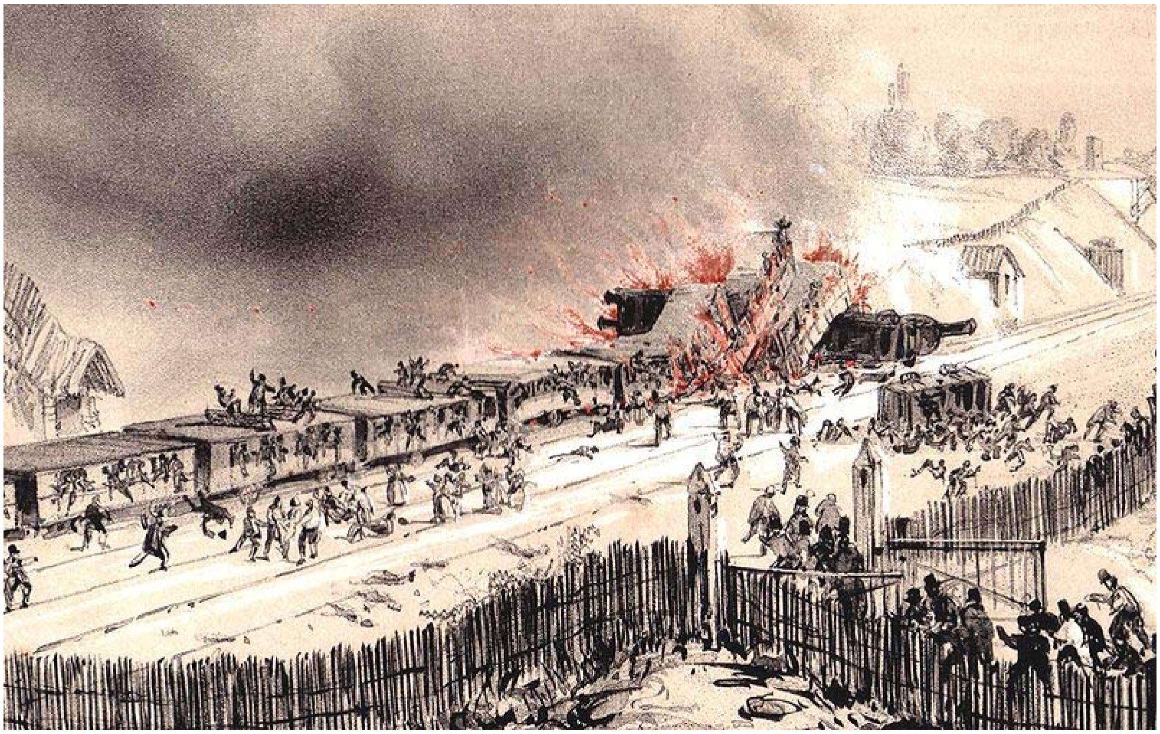
Fatigue cracks that have begun to propagate can sometimes be stopped by drilling holes, called *drill stops*, in the path of the fatigue crack. This is not recommended as a general practice because the hole represents a stress concentration factor which depends on the size of the hole and geometry. There is thus the possibility of a new crack starting in the side of the hole. It is always far better to replace the cracked part entirely.

Material change

Changes in the materials used in parts can also improve fatigue life. For example, parts can be made from better fatigue rated metals. Complete replacement and redesign of parts can also reduce if not eliminate fatigue problems. Thus helicopter rotor blades and propellers in metal are being replaced by composite equivalents. They are not only lighter, but also much more resistant to fatigue. They are more expensive, but the extra cost is amply repaid by their greater integrity, since loss of a rotor blade usually leads to total loss of the aircraft. A similar argument has been made for replacement of metal fuselages, wings and tails of aircraft.

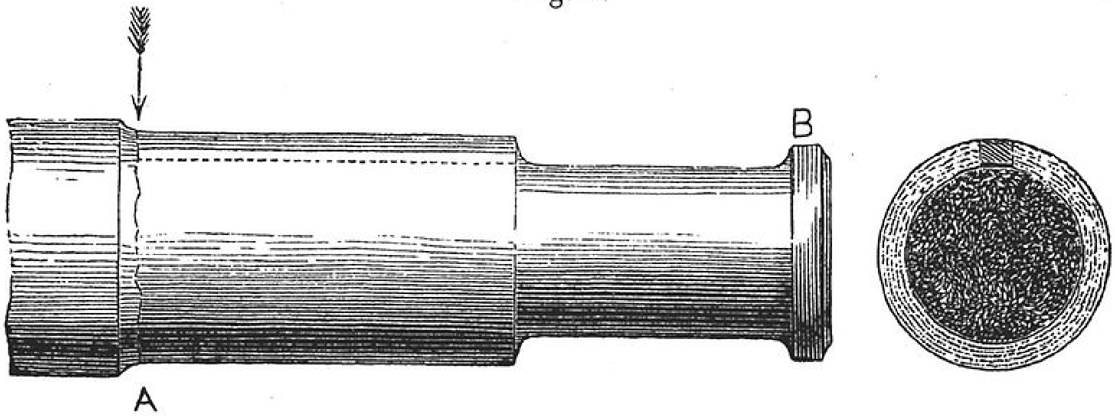
Infamous fatigue failures

Versailles train crash



Versailles train disaster

Fig. 1.

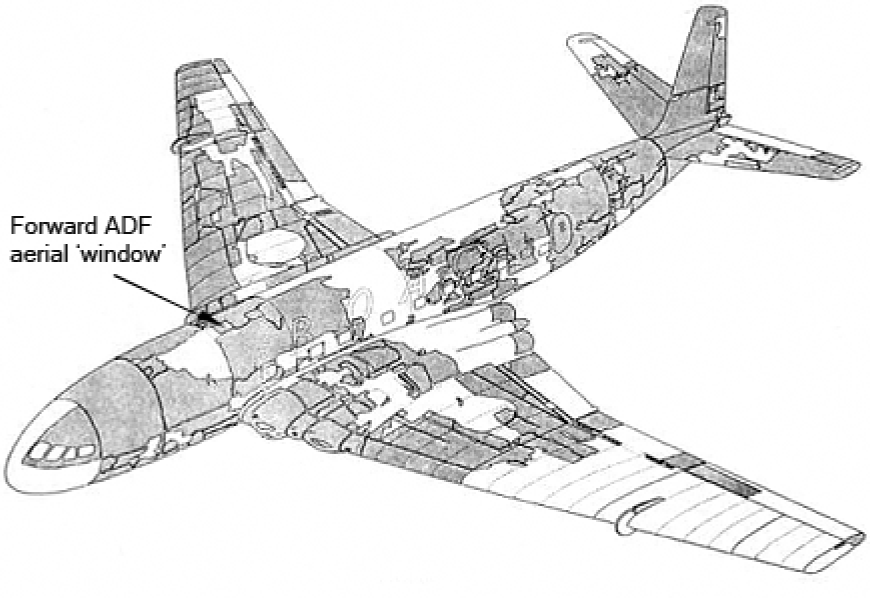


Drawing of a fatigue failure in an axle by Joseph Glynn, 1843.

Following the King's fete celebrations at the Palace of Versailles, a train returning to Paris crashed in May 1842 at Meudon after the leading locomotive broke an axle. The carriages behind piled into the wrecked engines and caught fire. At least 55 passengers were killed trapped in the carriages, including the explorer Jules Dumont d'Urville. This accident is known in France as the "Catastrophe ferroviaire de Meudon". The accident was witnessed by the British locomotive engineer Joseph Locke and widely reported in Britain. It was discussed extensively by engineers, who sought an explanation.

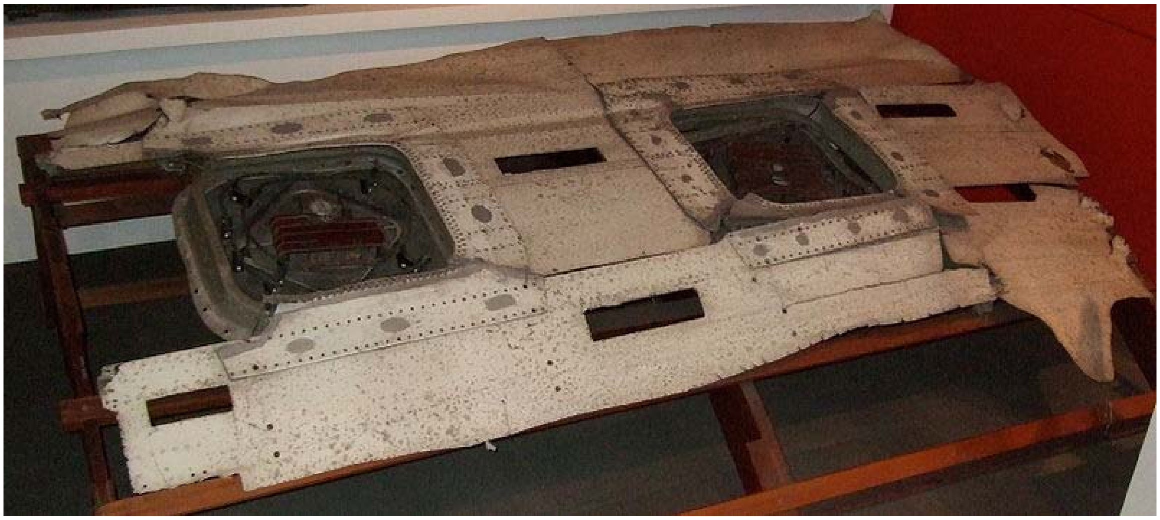
The derailment had been the result of a broken locomotive axle. Rankine's investigation of broken axles in Britain highlighted the importance of stress concentration, and the mechanism of crack growth with repeated loading. His and other papers suggesting a crack growth mechanism through repeated stressing, however, were ignored, and fatigue failures occurred at an ever increasing rate on the expanding railway system. Other spurious theories seemed to be more acceptable, such as the idea that the metal had somehow "crystallized". The notion was based on the crystalline appearance of the fast fracture region of the crack surface, but ignored the fact that the metal was already highly crystalline.

de Havilland Comet



The recovered (shaded) parts of the wreckage of *G-ALYP* and the site (arrowed) of the failure

Two de Havilland Comet passenger jets broke up in mid-air and crashed within a few months of each other in 1954. As a result systematic tests were conducted on a fuselage immersed and pressurised in a water tank. After the equivalent of 3,000 flights investigators at the Royal Aircraft Establishment (RAE) were able to conclude that the crash had been due to failure of the pressure cabin at the forward Automatic Direction Finder window in the roof. This 'window' was in fact one of two apertures for the aerials of an electronic navigation system in which opaque fibreglass panels took the place of the window 'glass'. The failure was a result of metal fatigue caused by the repeated pressurisation and de-pressurisation of the aircraft cabin. Another fact was that the supports around the windows were riveted, not bonded, as the original specifications for the aircraft had called for. The problem was exacerbated by the punch rivet construction technique employed. Unlike drill riveting, the imperfect nature of the hole created by punch riveting caused manufacturing defect cracks which may have caused the start of fatigue cracks around the rivet.

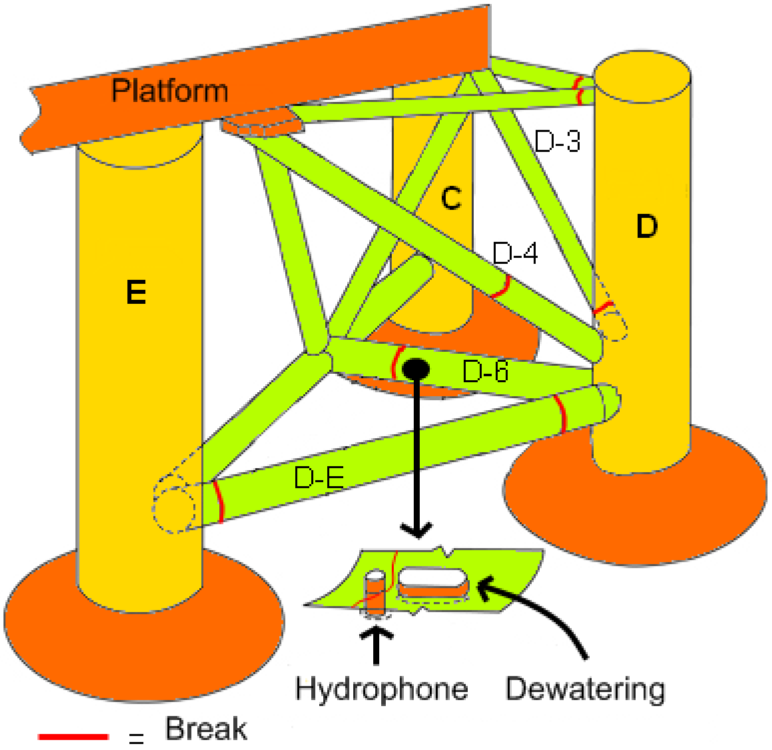


The fuselage fragment of *G-ALYP* on display in the Science Museum in London

The Comet's pressure cabin had been designed to a safety factor comfortably in excess of that required by British Civil Airworthiness Requirements (2.5 times the cabin proof pressure as opposed to the requirement of 1.33 times and an ultimate load of 2.0 times the cabin pressure) and the accident caused a revision in the estimates of the safe loading strength requirements of airliner pressure cabins.

In addition, it was discovered that the stresses around pressure cabin apertures were considerably higher than had been anticipated, especially around sharp-cornered cut-outs, such as windows. As a result, all future jet airliners would feature windows with rounded corners, the curve eliminating a stress concentration. This was a noticeable distinguishing feature of all later models of the Comet. Investigators from the RAE told a public inquiry that the sharp corners near the Comets' window openings acted as initiation sites for cracks. The skin of the aircraft was also too thin, and cracks from manufacturing stresses were present at the corners.

Alexander L. Kielland oil platform capsize



Fractures on the right side of the Alexander L. Kielland rig

The *Alexander L. Kielland* was a Norwegian semi-submersible drilling rig that capsized whilst working in the Ekofisk oil field in March 1980 killing 123 people. The capsize was the worst disaster in Norwegian waters since World War II. The rig, located approximately 320 km east from Dundee, Scotland, was owned by the Stavanger Drilling Company of Norway and was on hire to the U.S. company Phillips Petroleum at the time of the disaster. In driving rain and mist, early in the evening of 27 March 1980 more than 200 men were off duty in the accommodation on the *Alexander L. Kielland*. The wind was gusting to 40 knots with waves up to 12 m high. The rig had just been winched away from the *Edda* production platform. Minutes before 18:30 those on board felt a 'sharp crack' followed by 'some kind of trembling'. Suddenly the rig heeled over 30° and then stabilised. Five of the six anchor cables had broken, the one remaining cable preventing the rig from capsizing. The list continued to increase and at 18.53 the remaining anchor cable snapped and the rig turned upside down.

A year later in March 1981, the investigative report concluded that the rig collapsed owing to a fatigue crack in one of its six bracings (bracing D-6), which connected the collapsed D-leg to the rest of the rig. This was traced to a small 6 mm fillet weld which joined a non-load-bearing flange plate to this D-6 bracing. This flange plate held a sonar device used during drilling operations. The poor profile of the fillet weld contributed to a reduction in its fatigue strength. Further, the investigation found considerable amounts of lamellar tearing in the flange plate and cold cracks in the butt weld. Cold cracks in the welds, increased stress concentrations due to the weakened flange plate, the poor weld profile, and cyclical stresses (which would be common in the North Sea), seemed to collectively play a role in the rig's collapse.

Others

- The 1919 Boston Molasses Disaster has been attributed to a fatigue failure.
- The 1957 "Mt. Pinatubo", presidential plane of Philippine President Ramon Magsaysay, crashed due to engine failure caused by metal fatigue.
- The 1968 Los Angeles Airways Flight 417 lost one of its main rotor blades due to fatigue failure.
- The 1985 Japan Airlines Flight 123 crashed after the aircraft lost its vertical stabilizer due to faulty repairs on the rear bulkhead.
- The 1988 Aloha Airlines Flight 243 suffered an explosive decompression due to fatigue failure.
- The 1989 United Airlines Flight 232 lost its tail engine due to fatigue failure.
- The 1992 El Al Flight 1862 lost both engines on its right-wing due to fatigue failure with the #3 Engine.
- The 1998 Eschede train disaster was caused by fatigue failure of a single composite wheel.
- The 2002 China Airlines Flight 611 had disintegrated in-flight due to fatigue failure.
- The 2005 Chalk's Ocean Airways Flight 101 lost its right wing due to fatigue failure brought about by inadequate maintenance practices.

Chapter 8

Liquid Metal Embrittlement and Photo-Oxidation of Polymers

Liquid metal embrittlement

Liquid metal embrittlement is a phenomenon of practical importance, where certain ductile metals experience drastic loss in tensile ductility or undergo brittle fracture when tested in the presence of specific liquid metals. Generally, a tensile stress, either externally applied or internally present, is needed to induce embrittlement. Exceptions to this rule have been observed, as in the case of aluminium in the presence of liquid gallium. People have studied this phenomenon from the beginning of the 20th century. Many of its phenomenological characteristics are known and several mechanisms were proposed to explain it. The practical significance of liquid metal embrittlement is revealed by the observation that several steels experienced ductility losses and cracking during hot dip galvanizing or during subsequent fabrication.

Liquid metal embrittlement effects can be observed even in solid state, when one of the metals is brought close to its melting point; eg. cadmium-coated parts operating at high temperature.

Characteristics

Mechanical behaviour

Liquid metal embrittlement or LME is characterized by the reduction in the true fracture stress and/or in the strain to fracture when tested in the presence of liquid metals as compared to that obtained in air / vacuum tests. The reduction in fracture strain is generally temperature dependent and a “ductility trough” is observed as the test temperature is decreased. A ductile-to-brittle transition behaviour is also exhibited by many metal couples. The shape of the elastic region of the stress-strain curve is not altered, but the plastic region may be changed during LME. Very high crack propagation rates, varying from few centimeters per second to several meters per second are induced in solid metals by the embrittling liquid metals. An incubation period and a slow pre-critical crack propagation stage generally precede final fracture.

Metal chemistry

It is believed that there is specificity in the solid-liquid metals combinations experiencing LME. There should be limited mutual solubilities for the metal couple to cause embrittlement. Excess solubility makes sharp crack propagation difficult, but no solubility condition prevents wetting of the solid surfaces by liquid metal and prevents LME. Presence of an oxide layer on the solid metal surface also prevents good contact between the two metals and stops LME. The chemical compositions of the solid and liquid metals affect the severity of embrittlement. Addition of third elements to the liquid metal may increase or decrease the embrittlement and alters the temperature region over which embrittlement is seen. Metal combinations which form intermetallic compounds do not cause LME.

Metallurgy

Alloying of the solid metal alters its LME. Some alloying elements may increase the severity while others may prevent LME. The action of the alloying element is known to be segregation to grain boundaries of the solid metal and altering the grain boundary properties. Accordingly, maximum LME is seen in cases where alloy additions elements have saturated the grain boundaries of the solid metal. The hardness and deformation behaviour of the solid metal affect its susceptibility to LME. Generally harder metals are more severely embrittled. Grain size greatly influences LME. Solids with larger grains are more severely embrittled and the fracture stress varies inversely with the square root of grain diameter. Also the brittle to ductile transition temperature is increased by increasing grain size.

Physico-chemical properties

The interfacial energy between the solid and liquid metals and the grain boundary energy of the solid metal greatly influence LME. These energies depend upon the chemical compositions of the metal couple.

Test parameters

External parameters like temperature, strain rate, stress and time of exposure to the liquid metal prior to testing affect LME. Temperature produces a ductility trough and a ductile to brittle transition behaviour in the solid metal. The temperature range of the trough as well as the transition temperature are altered by the composition of the liquid and solid metals, the structure of the solid metal and other experimental parameters. The lower limit of the ductility trough generally coincides with the melting point of the liquid metal.

The upper limit is strain rate sensitive. Temperature also affects the kinetics of LME. An increase in strain rate increases the upper limit temperature as well as the crack propagation rate. In most metal couples LME does not occur below a threshold stress level.

Mechanisms

Many theories have been proposed for LME. The major ones are listed below;

- The dissolution-diffusion model of Robertson and Glickman says that adsorption of the liquid metal on the solid metal induces dissolution and inward diffusion. Under stress these processes lead to crack nucleation and propagation.
- The brittle fracture theory of Stoloff and Johnson, Westwood and Kamdar proposed that the adsorption of the liquid metal atoms at the crack tip weakens inter-atomic bonds and propagates the crack.
- Gordon postulated a model based on diffusion-penetration of liquid metal atoms to nucleate cracks which under stress grow to cause failure.
- The ductile failure model of Lynch and Popovich predicted that adsorption of the liquid metal leads to weakening of atomic bonds and nucleation of dislocations which move under stress, pile-up and work harden the solid. Also dissolution helps in the nucleation of voids which grow under stress and cause ductile failure.

All of these models utilize the concept of an adsorption-induced surface energy lowering of the solid metal as the central cause of LME. They succeeded in predicting many of the phenomenological observations. However, a quantitative prediction of LME is still elusive.

Mercury embrittlement

The most common liquid metal causing embrittlement is mercury. Its spills present especially significant danger for airplanes. The aluminium-zinc-magnesium-copper alloy DTD 5050B is especially susceptible. The Al-Cu alloy DTD 5020A is less susceptible. Elemental mercury spilled can be immobilized and made relatively harmless by silver nitrate.

On 1 January 2004, the Moomba, South Australia, natural gas processing plant operated by Santos suffered a major fire. The gas release that led to the fire was caused by the failure of a heat exchanger (cold box) inlet nozzle in the liquids recovery plant. The failure of the inlet nozzle was due to liquid metal embrittlement of the train B aluminium cold box by elemental mercury.

Photo-oxidation of polymers

Photo-oxidation is the degradation of a polymer surface in the presence of oxygen or ozone. The effect is facilitated by radiant energy such as UV or artificial light. This process is the most significant factor in weathering of polymers. Photo-oxidation is a chemical change that reduces the polymer's molecular weight. As a consequence of this change the material becomes more brittle, with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation. High temperature and localised stress concentrations are factors that significantly increase the effect of photo-oxidation.

Photo-oxidation protection

Poly(ethylene-naphthalate) (PEN) can be protected by applying a zinc oxide coating, which acts as protective film reducing the diffusion of oxygen. Zinc oxide can also be used on polycarbonate (PC) to decrease the oxidation and photo-yellowing rate caused by solar radiation.

Effects of dyes/pigments

Adding pigment light absorbers and photostabilizers, (UV absorbers), are one way to minimise photo-oxidation in polymers. Antioxidants are used to inhibit the formation of hydroperoxides in the photo-oxidation process.

Dyes and pigments are used in polymer materials to provide color changing properties. These additives can reduce the rate of polymer degradation. Cu-phthalocyanine dye can help stabilize against degradation, but in other situations such as photochemical aging can actually accelerate degradation. The excited Cu-phthalocyanine may abstract hydrogen atoms from methyl groups in the PC, which increase the formation of free radicals. This acts as the starting points for the sequential photo-oxidation reactions leading to the degradation of the PC.

Electron transfer sensitization is a mechanism where the excited Cu-phthalocyanine abstracts electrons from PC to form Cu-Ph radical anion and PC radical cations. These species in the presence of oxygen can cause oxidation of the aromatic ring.

Chemical mechanism

Aldehydes, ketones and carboxylic acids along or at the end of polymer chains are generated by oxygenated species in photolysis of photo-oxidation. The initiation of photo-oxidation reactions is due to the existence of chromophoric groups in the macromolecules. Photo-oxidation can occur simultaneously with thermal degradation and either one of these effects can accelerate the other.

The photo-oxidation reactions include chain scission, cross linking and secondary oxidative reactions. The following process steps can be considered:

1. Initial step: Free radical formation can be formed by light photon absorption.
2. Chain Propagation step: The free radical reacts with oxygen to produce polymer peroxy radicals (POO•) and generate polymer hydroperoxide (POOH) and new polymer alkyl radical (P•).
3. Chain Branching: The formation of polymer oxy radicals (PO•) and hydroxy radicals (HO•) can be formed by photolysis.
4. Termination step: Cross linking is a result of the reaction of different free radicals with each other.

$$Polymer \longrightarrow P\bullet + P\bullet \qquad \text{Initial step}$$

$$\begin{array}{ll} P\bullet + O_2 \longrightarrow POO\bullet & \\ POO\bullet + PH \longrightarrow POOH + P\bullet & \end{array} \qquad \text{Chain Propagation}$$

$$\begin{array}{l} POOH \longrightarrow PO\bullet + \bullet OH \\ PH + \bullet OH \longrightarrow P\bullet + H_2O \\ PO\bullet \longrightarrow \text{Chain scisson reactions} \end{array} \qquad \text{Chain branching}$$

$$\left.\begin{array}{l} POO\bullet + POO\bullet \\ POO\bullet + P\bullet \\ P\bullet + P\bullet \end{array}\right\} \longrightarrow \begin{array}{l}\text{Cross linking} \\ \text{reactions to non-} \\ \text{radical products}\end{array} \qquad \text{Termination}$$

where PH = Polymer

P• = Polymer alkyl radical

PO• = Polymer oxy radical (Polymer alkoxy radical)

POO• = Polymer peroxy radical (Polymer alkylperoxy radical)

POOH = Polymer hydroperoxide

HO• = hydroxy radical

Chapter 9

Polymer Degradation

Polymer degradation is a change in the properties - tensile strength, colour, shape, etc. - of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. The changes in properties are often termed "aging".

In a finished product such a change is to be prevented or delayed. Degradation can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. Degradation can also be induced deliberately to assist structure determination.

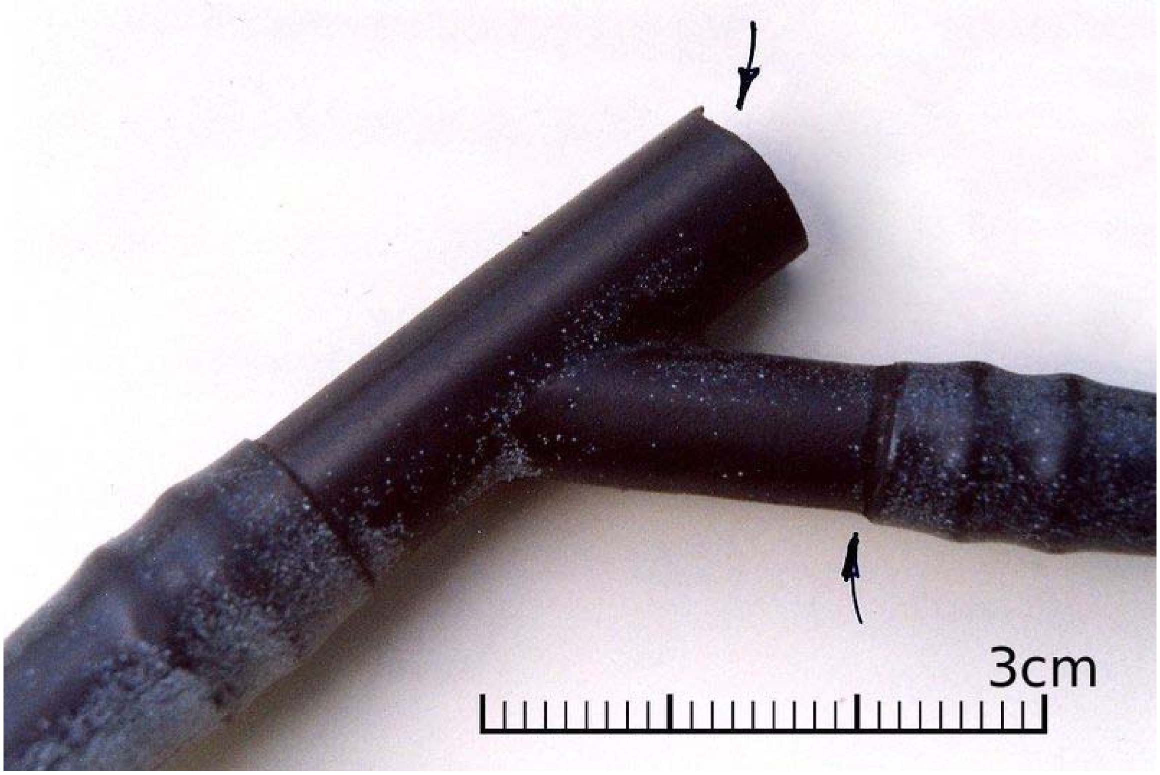
Polymeric molecules are very large (on the molecular scale), and their unique and useful properties are mainly a result of their size. Any loss in chain length lowers tensile strength and is a primary cause of premature cracking.

Commodity polymers

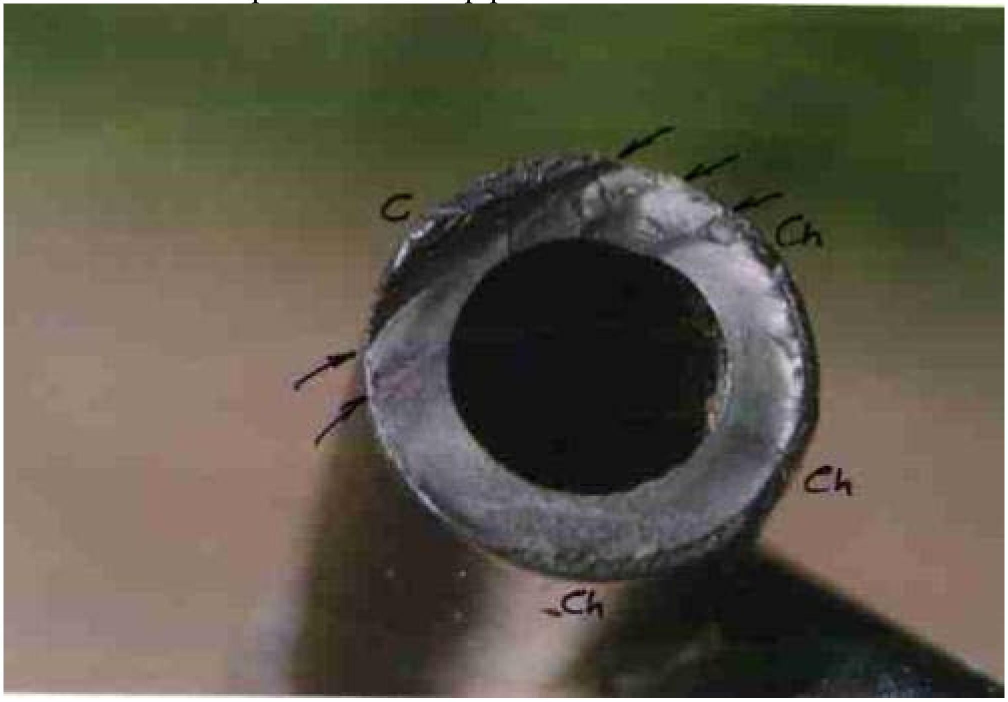
Today there are primarily seven commodity polymers in use: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate or PET, polystyrene, polycarbonate, and poly(methyl methacrylate) (Plexiglass). These make up nearly 98% of all polymers and plastics encountered in daily life. Each of these polymers has its own characteristic modes of degradation and resistances to heat, light and chemicals. Polyethylene, polypropylene, and poly(methyl methacrylate) are sensitive to oxidation and UV radiation, while PVC may discolour at high temperatures due to loss of hydrogen chloride gas, and become very brittle. PET is sensitive to hydrolysis and attack by strong acids, while polycarbonate depolymerizes rapidly when exposed to strong alkalis.

For example, polyethylene usually degrades by *random scission* - that is by a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When this polymer is heated above 450 Celsius it becomes a complex mixture of molecules of various sizes that resemble gasoline. Other polymers - like polyalphamethylstyrene -

undergo 'unspecific' chain scission with breakage occurring only at the ends; they literally unzip or depolymerize to become the constituent monomers.



Close-up of broken fuel pipe from road traffic accident



Close-up of broken fuel pipe connector

Photoinduced degradation

Most polymers can be degraded by photolysis to give lower molecular weight molecules. Electromagnetic waves with the energy of visible light or higher, such as ultraviolet light, X-rays and gamma rays are usually involved in such reactions.

Thermal degradation

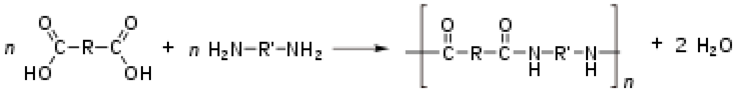
Chain-growth polymers like poly(methyl methacrylate) can be degraded by thermolysis at high temperatures to give monomers, oils, gases and water. The degradation takes place by:

Thermolysis type	Added material	Temperature	Pressure	Final product
Pyrolysis		Around 500°C	Reduced pressure	
Hydrogenation	Dihydrogen	Around 450°C	Around 200 bars	
Gasification	Dioxygen and/or water		Under pressure	Carbon monoxide, Carbon dioxide and hydrogen

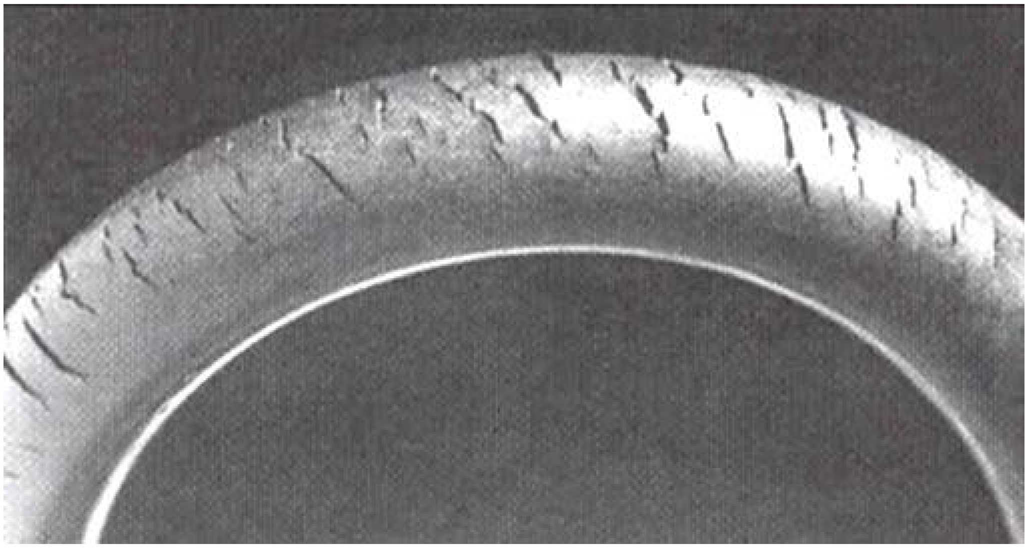
Chemical degradation

Solvolysis

Step-growth polymers like polyesters, polyamides and polycarbonates can be degraded by solvolysis and mainly hydrolysis to give lower molecular weight molecules. The hydrolysis takes place in the presence of water containing an acid or a base as catalyst. Polyamide is sensitive to degradation by acids and polyamide mouldings will crack when attacked by strong acids. For example, the fracture surface of a fuel connector showed the progressive growth of the crack from acid attack (Ch) to the final cusp (C) of polymer. The problem is known as stress corrosion cracking, and in this case was caused by hydrolysis of the polymer. It was the reverse reaction of the synthesis of the polymer:



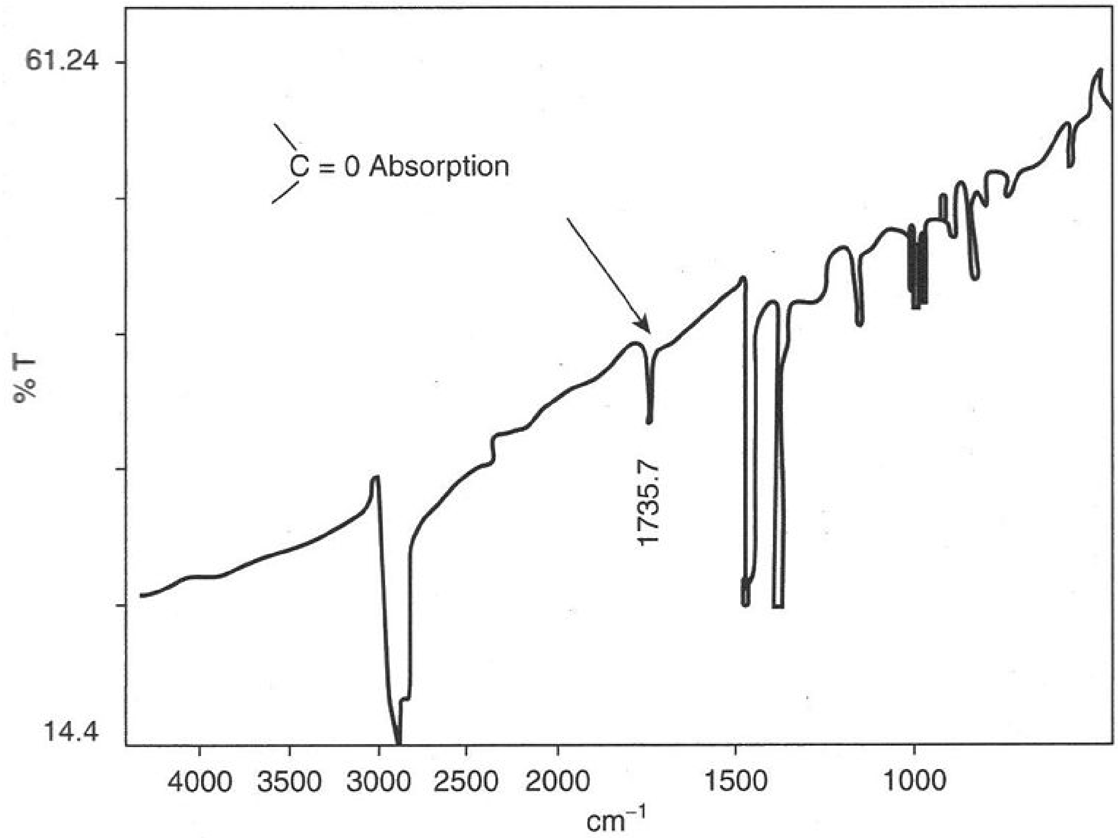
Ozonolysis



Ozone cracking in Natural rubber tubing

Cracks can be formed in many different elastomers by ozone attack. Tiny traces of the gas in the air will attack double bonds in rubber chains, with Natural rubber, polybutadiene, Styrene-butadiene rubber and NBR being most sensitive to degradation. Ozone cracks form in products under tension, but the critical strain is very small. The cracks are always oriented at right angles to the strain axis, so will form around the circumference in a rubber tube bent over. Such cracks are dangerous when they occur in fuel pipes because the cracks will grow from the outside exposed surfaces into the bore of the pipe, and fuel leakage and fire may follow. The problem of ozone cracking can be prevented by adding anti-ozonants to the rubber before vulcanization. Ozone cracks were commonly seen in automobile tire sidewalls, but are now seen rarely thanks to these additives. On the other hand, the problem does recur in unprotected products such as rubber tubing and seals.

Oxidation



IR spectrum showing carbonyl absorption due to oxidative degradation of polypropylene crutch moulding

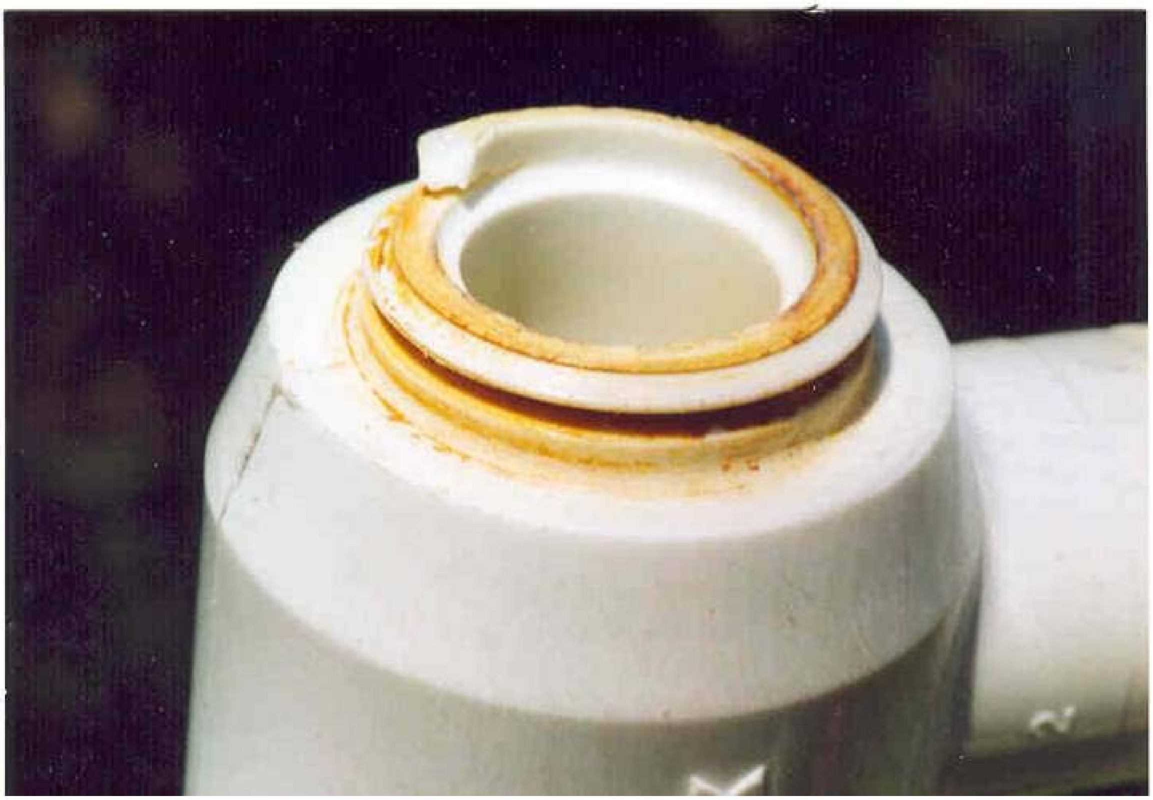
Polymers are susceptible to attack by atmospheric oxygen, especially at elevated temperatures encountered during processing to shape. Many process methods such as extrusion and injection moulding involve pumping molten polymer into tools, and the high temperatures needed for melting may result in oxidation unless precautions are taken. For example, a forearm crutch suddenly snapped and the user was severely injured in the resulting fall. The crutch had fractured across a polypropylene insert within the aluminium tube of the device, and infra-red spectroscopy of the material showed that it had oxidised, possible as a result of poor moulding.

Oxidation is usually relatively easy to detect owing to the strong absorption by the carbonyl group in the spectrum of polyolefins. Polypropylene has a relatively simple spectrum with few peaks at the carbonyl position (like polyethylene). Oxidation tends to start at tertiary carbon atoms because the free radicals formed here are more stable and longer lasting, making them more susceptible to attack by oxygen. The carbonyl group can be further oxidised to break the chain, this weakens the material by lowering its molecular weight, and cracks start to grow in the regions affected.

Galvanic action

Polymer degradation by galvanic action was first described in the technical literature in 1990.. This was the discovery that "plastics can corrode", i.e. polymer degradation may occur through galvanic action similar to that of metals under certain conditions. Normally, when two dissimilar metals such as copper (Cu) and iron (Fe) are put into contact and then immersed in salt water, the iron will undergo corrosion, or rust. This is called a galvanic circuit where the copper is the noble metal and the iron is the active metal, i.e., the copper is the cathode or positive (+) electrode and the iron is the anode, or negative (-) electrode. A battery is formed. It follows that plastics are made stronger by impregnating them with thin carbon fibers only a few micrometers in diameter known as carbon fiber reinforced polymers (CFRP). This is to produce materials that are high strength and resistant to high temperatures. The carbon fibers act as a noble metal similar to gold (Au) or platinum (Pt). When put into contact with a more active metal, for example with aluminum (Al) in salt water the aluminum corrodes. However in early 1990, it was reported that imide-linked resins in CFRP composites degrade when bare composite is coupled with an active metal in salt water environments. This is because corrosion not only occurs at the aluminum anode, but also at the carbon fiber cathode in the form of a very strong base with a pH of about 13. This strong base reacts with the polymer chain structure degrading the polymer. Polymers affected include bismaleimides (BMI), condensation polyimides, triazines, and blends thereof. Degradation occurs in the form of dissolved resin and loose fibers. The hydroxyl ions generated at the graphite cathode attack the O-C-N bond in the polyimide structure. Standard corrosion protection procedures were found to prevent polymer degradation under most conditions.

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 US as a result of chlorine-induced cracking. In essence, the gas attacks sensitive parts of the chain molecules (especially secondary, tertiary, or allylic carbon atoms), oxidizing 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. Discolouration 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. The problems in the US also occurred to polybutylene pipework, and led to the material being removed from that market, although it is still used elsewhere in the world.

Biological degradation

Biodegradable plastics can be biologically degraded by microorganisms to give lower molecular weight molecules. To degrade properly biodegradable polymers need to be treated like compost and not just left in a landfill site where degradation is very difficult due to the lack of oxygen and moisture.

Stabilisers

Hindered amine light stabilisers (HALS) stabilise against weathering by scavenging free radicals that are produced by photo-oxidation of the polymer matrix. UV-absorbers stabilises against weathering by absorbing ultraviolet light and converting it into heat. Antioxidants stabilize the polymer by terminating the chain reaction due to the absorption of UV light from sunlight. The chain reaction initiated by photo-oxidation leads to cessation of crosslinking of the polymers and degradation the property of polymers.

Chapter 10

Thermal Degradation of Polymers and Thermo Mechanical Fatigue

Thermal degradation of polymers

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties.

The Mechanism of Thermal Degradation

Most types of degradation follow a similar basic pattern. The conventional model for thermal degradation is that of an autoxidation process which involves the major steps of initiation, propagation, branching, and termination.

Initiation

The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain as a result of energy input from heat or light. This creates a highly reactive and unstable polymer ‘free radical’ (R•) and a hydrogen atom with an unpaired electron (H•).

Propagation

The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical (R•) reacts with an oxygen (O_2) molecule to form a peroxy radical (ROO•) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide (ROOH) and so regenerate the free radical (R•). The hydroperoxide can then split into two new free radicals, (RO•) + (•OH), which will continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain.

Termination

The termination of thermal degradation is achieved by ‘mopping up’ the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the plastic.

The Research Methods of Thermal Degradation of Polymers

TGA

(Thermogravimetric Analysis) (TGA) refers to the techniques where a sample is heated in a controlled atmosphere at a defined heating rate whilst the samples mass is measured. When a polymer sample degrades, its mass decreases due to the production of gaseous products like carbon monoxide, water vapour and carbon dioxide.

DTA and DSC

(Differential thermal analysis) (DTA) and (differential scanning calorimetry) (DSC): Analyzing the heating effect of polymer during the physical changes in terms of glass transition, melting, and so on. These techniques measure the heat flow associated with oxidation.

Ways of Polymer Thermal Degradation

Depolymerisation

Under thermal effect, the end of polymer chain departs, and forms low free radical which has low activity. Then according to the chain reaction mechanism, the polymer loses the monomer one by one. However, the molecular chain doesn’t change a lot in a short time. The reaction is shown below. This process is common for polymethymethacrylate (perspex).

CH_2-$C(CH_3)COOCH_3$-CH_2-$C^*(CH_3)COOCH_3 \rightarrow CH_2$-$C^*(CH_3)COOCH_3$ + $CH_2=C(CH_3)COOCH_3$

Random Chain Scission

The backbone will be break down randomly, could be occurred at any position of the backbone. The molecular weight decreases rapidly, and cannot get monomer in this reaction, this is because it forms new free radical which has high activity can occurs intermolecular chain transfer and disproportion termination with the CH2'group.

CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$CH_2' \rightarrow CH_2$-CH_2-$CH=CH_2$ + CH_3-CH_2-CH_2' or $CH_2'+CH_2=CH$-CH_2-CH_2-CH_2-CH_3

Side-Group Elimination

Groups that are attached to the side of the backbone are held by bonds which are weaker than the bonds connecting the chain. When the polymer was being heated, the side groups are stripped off from the chain before it is broken into smaller pieces. For example the PVC eliminates HCL, under 100-120^{o}C.

$CH_2(Cl)CHCH_2CH(Cl) \rightarrow CH=CH$-$CH=CH+2HCl$

Oxidation of the polymer

Polyphenylene oxide is well known for oxidation.

Thermo mechanical fatigue

Thermo Mechanical Fatigue (TMF) is a variation of mechanical fatigue of materials where heating and cooling cycles are applied to a test material additional to a mechanical cyclic loading. The temperature cycles have - in most cases - the same frequency as the loading cycles, but have different phase shifts.

If the phase shift is δ=0 the TMF tests are called in-phase tests, i. e. a tensile force is applied to the specimen while heating is done. If the phase shift is δ=180° the TMF test are called out-of-phase tests, i. e. the sample is cooled while in tension. For special testing parameters the phase shift can be applied between $360° > \delta > 0$, to fit the real requirements for the tested material in later application fields.

Application

TMF testing is mainly done, to determine the total lifetime of technical components (e. g. turbine blades of aeroplane engines (jet engines) and gas turbines) previous to the technical implementation of that part. The material is tested with parameters (i. e. given temperature range, given maximum forces or stresses, cooling rates, phase shifts, etc.)

that resemble the later usage profile of that material. So it is made sure, that the material can withstand the later technical requirements. The TMF test results are used (among other test results) to determine the total lifetime of a part as well as maintenance intervals for aeroplanes.

Comparison of TMF tests

TMF tests need to be done, because the results cannot be predicted from isothermal mechanical fatigue tests. Many materials undergo a recovery process at high temperatures, and some material coatings have a ductile to brittle transition in the temperature range, that affect the total lifetime of a sample a lot. TMF test results cannot be compared with other TMF results either, if one of the testing parameter differs, like e. g. temperature range, cooling rate, applied forces or stresses, phase shift.

Chapter 11

UV Degradation and Weather Testing of Polymers

UV degradation

Many natural and synthetic polymers are attacked by ultra-violet radiation and products made using these materials may crack or disintegrate (that is,if they are not UV-stable). The problem is known as *UV degradation*, and is a common problem in products exposed to sunlight. Continuous exposure is a more serious problem than intermittent exposure, since attack is dependent on the extent and degree of exposure.

Many pigments and dyes can also be affected, when the problem is known as phototendering in textiles such as curtains or drapes.

Susceptible polymers

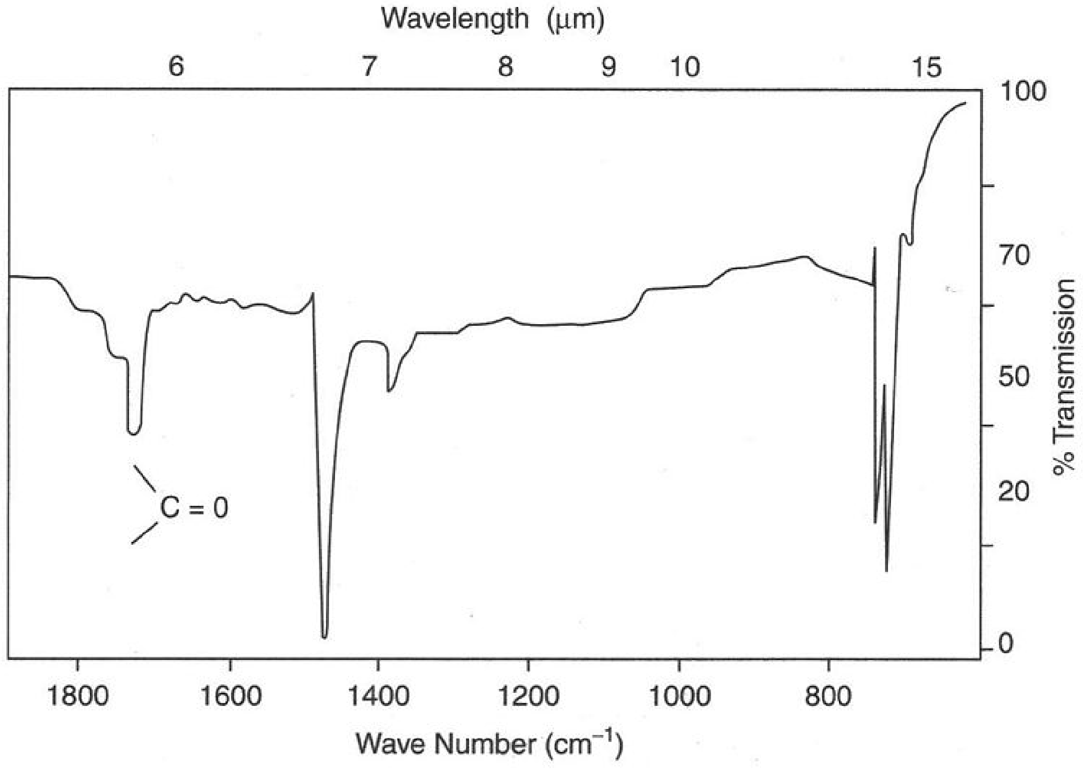
Effect of UV exposure on polypropylene rope

Common synthetic polymers which may be attacked include polypropylene and LDPE where tertiary carbon bonds in their chain structures are the centres of attack. The ultra-violet rays activate such bonds to form free radicals, which then react further with oxygen in the atmosphere, producing carbonyl groups in the main chain. The exposed surfaces of products may then discolour and crack, although in bad cases, complete product disintegration can occur.

In fibre products like rope used in outdoor applications, product life will be low because the outer fibres will be attacked first, and will easily be damaged by abrasion for example. Discolouration of the rope may also occur, so giving an early warning of the problem.

Polymers which possess UV-absorbing groups such as aromatic rings may also be sensitive to UV degradation. Aramid fibres like Kevlar for example are highly UV sensitive and must be protected from the deleterious effects of sunlight.

Detection



IR spectrum showing carbonyl absorption due to UV degradation of polyethylene

The problem can be detected before serious cracks are seen in a product using infra-red spectroscopy, where attack occurs by oxidation of bonds activated by the UV radiation forming carbonyl groups in the polymer chains.

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 made by rotational moulding in LDPE, which had cracked prematurely in service. Many similar cones also failed because an anti-UV additive had not been used during processing. Other plastic products which failed included polypropylene mancabs used at roadworks which cracked after service of only a few months.

Prevention

UV attack by sunlight can be ameliorated or prevented by adding anti-UV chemicals to the polymer when mixing the ingredients, prior to shaping the product by injection moulding for example.

UV Stabilizers in plastics usually act by absorbing the UV radiation preferentially, and dissipating the energy as low level heat. The chemicals used are similar to those used in sunscreen cosmetic products, which protect skin from UV attack.

UV degradation in material testing

The effects of UV degradation on materials that require a long service life can be measured with accelerated exposure tests. With modern solar concentrator technologies it’s possible to simulate 63 years of natural UV radiation exposure on a test device in a single year. In Solar Power Modules degradation is a longterm issue according to material testings; the efficiency loss by UV degradation is about 6.81 to 9.54 % in 20 years.

Weather testing of polymers

Weather testing of polymers is the controlled polymer degradation and polymer coating degradation under lab or natural conditions.

Just like erosion of rocks, natural phenomena can cause degradation in polymer systems. The elements of most concern to polymers are Ultraviolet radiation, moisture and humidity, high temperatures and temperature fluctuations. Polymers are used in every day life, so it is important for scientists and polymer producers to understand durability and expected lifespan of polymer products. Paint, a common polymer coating, is used to change the colour, change the reflectance (gloss), as well as forming a protective coating. The structure of paint consists of pigments in a matrix of resin. A typical example is painted steel roofing and walling products, which are constantly exposed to harmful weathering conditions.

Typical result of polymer surface after weathering

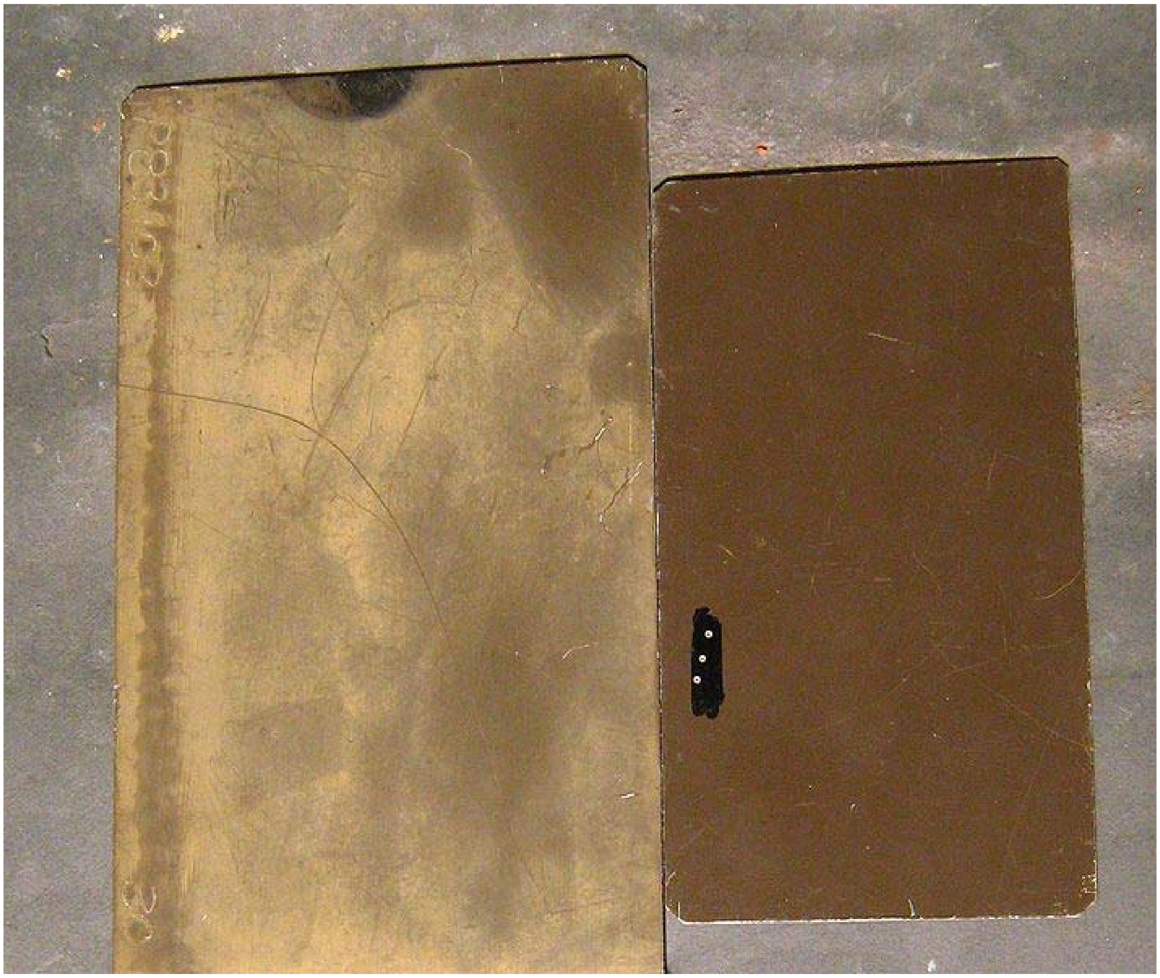


Figure 1.1: Weathered and unweathered samples of painted steel. Note the colour change.

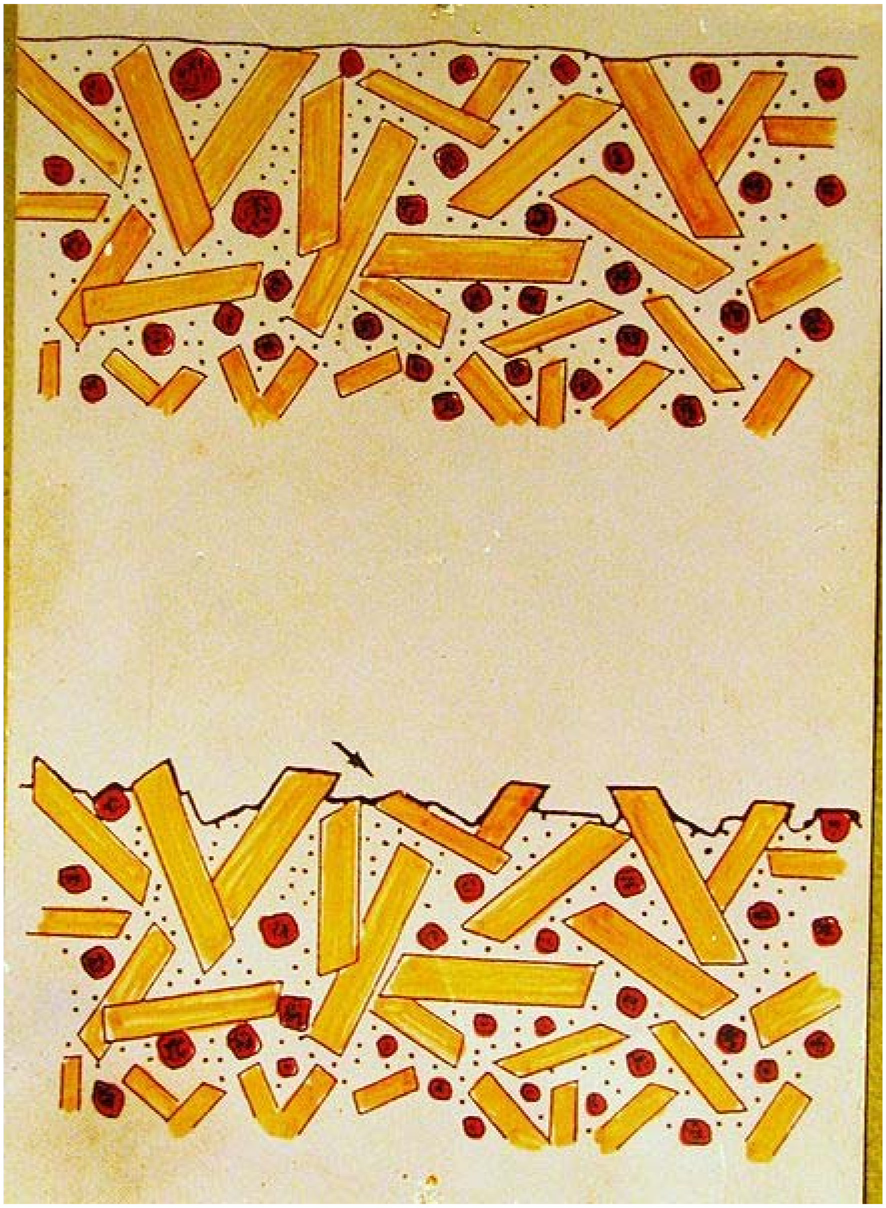


Figure 1.2: Diagram showing paint pigments in a resin matrix. It can be seen that weathering only removes the smaller pigments, resulting in the colour change

Figure 1.1 shows typical weathering results of a sample of painted steel; the paint on the steel is an example of a common polymer system. The sample on the left had been placed in an outdoor exposure rack, and weathered for a total of 6 years. It can be seen that the sample has a chalky appearance and has undergone a colour change in comparison to the unweathered sample on the right.

Colour is determined by light-reflecting chemical particles, pigments, in the paint. These particles can have very different physical sizes, as shown in the diagram in figure 1.2. In this example, the black pigments are the small black dots; red pigments are larger spheres, while the yellow pigments are acicular. This combination of pigments produces the original brown colour. The upper diagram has had no weathering, and the surface is still smooth and undamaged. The lower diagram shows the painted surface after weathering has occurred. The surface has eroded with significant loss of the black and red pigments from the surface layer. The pitted surface scatters light, therefore reducing the gloss and creating the chalky affect. The larger acicular yellow pigments are more difficult to remove, resulting in a colour change towards a more yellowy appearance. Weather testing was paramount in discovering this mechanism. Pigment composition has recently been modified to help minimise this effect.

Types of weather testing

There are 3 main testing techniques; Natural Weathering, Accelerated Natural Weathering and Artificial Weathering. Because natural weathering can be a slow process, each of the techniques is a tradeoff between realistic weathering results and the duration of testing before results are collated.

Natural weathering

A typical natural weather testing rack. This one is located in Bellambi, NSW, Australia

Natural Weathering involves placing samples on inclined racks oriented at the sun. In Northern hemisphere these racks are at an angle of 45 degrees in a southerly direction. In

Southern hemisphere these racks are at an angle of 45 degrees in a northerly direction. This angle ensures exposure to the full spectrum of solar radiation, from infrared to Ultra violet. Sites used for this type of testing are usually in tropical areas as high temperature, UV intensity and humidity are needed for maximum degradation. Florida, for example is the world standard as it possesses all three characteristics. Despite the harsh conditions, testing takes several years before significant results are achieved.

Accelerated natural weathering

To speed up the weathering process while still using natural weather conditions, accelerated natural testing can be applied. One method uses mirrors to amplify available UV radiation. A device known as a Fresnel-reflecting concentrator uses photo-receptor cells to maintain alignment with the sun and 10 mirrors to reflect sunlight onto the test specimens. With the latest technology for ultra-accelerated exposure testing it's possible to simulate 63 years of UV radiation exposure in a single year.

Such devices, which are known by trade names Acuvex, Q-Trac, and Emma, are typically used in Arizona and other desert locations with a high percentage of sunlight and low relative humidity. The Arizona desert typically provides 180 kilo-Langley per year. These exposures can be used with water spray to simulate a more humid climate. In addition, water containing up to 5% sodium chloride can be sprayed to create the conditions for corrosion to occur.

It is typical for this to accelerate weathering by a factor 5, in comparison to weathering in Florida.

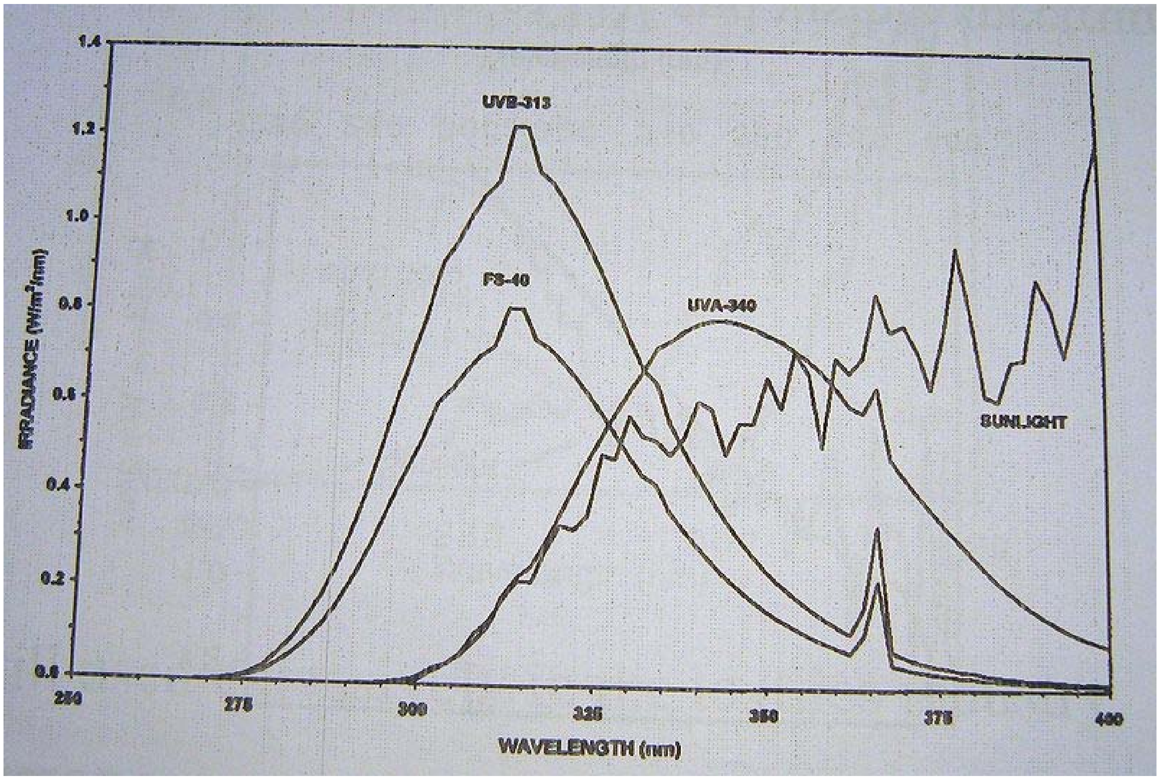
An Atrac in Townsville Australia, uses follow the sun technology in which the samples are rotated so that they always face the sun. In 17 months this produced the equivalent of 2 years of weathering.

A variety of environmental chambers are also used in conjunction with industry standards.

Artificial weathering

The weather testing process can be greatly accelerated through the use of specially designed weathering chambers. While this speeds up the time needed to get results, the conditions are not always representative of real world conditions. Most of the commercialized devices are using Gas-discharge lamp or Electric arc (carbon) to simulate/accelerate the effect of sunlight. Besides fluorescent lamps where the short UV are converted into visible light with fluorescent coatings, xenon, mercury, metal halide or carbon arc lamps have to be used with a careful elimination of shorter wavelenghs usually by adding a borosilicate filter.

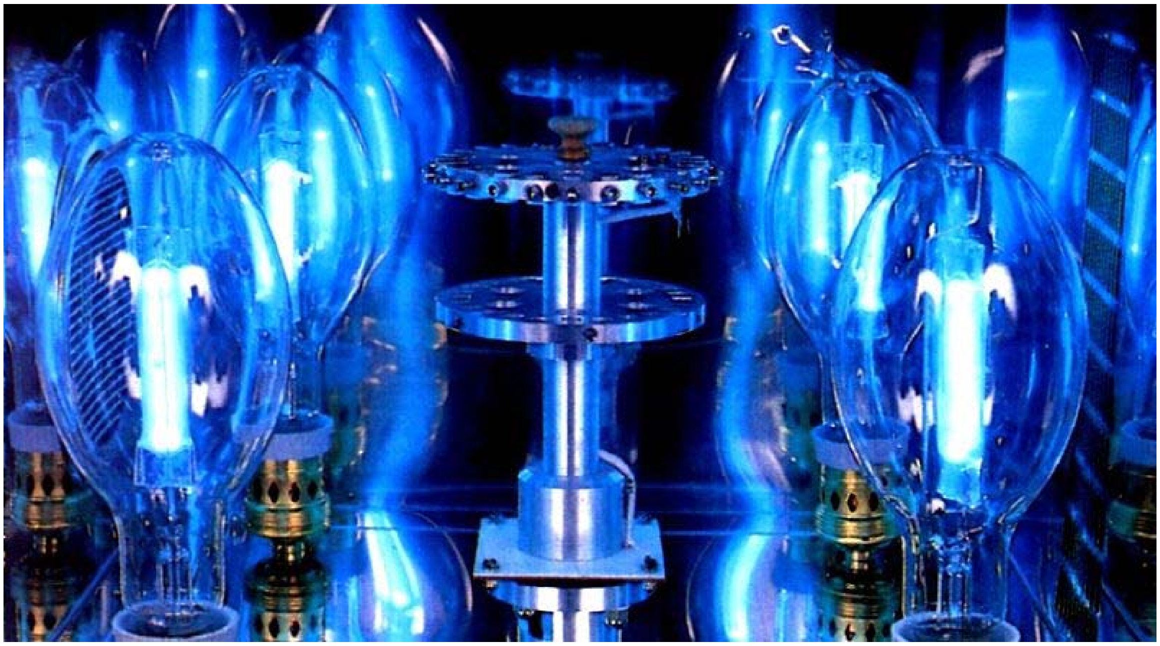
QUV



A graph comparing the wavelengths of UVA and UVB with those found in natural sunlight

QUV Accelerated Weathering testing is a laboratory simulation of the damaging forces of weather for the purposes of predicting the relative durability of materials exposed to outdoor environments. Racks of samples are placed in the QUV chamber. Rain and dew systems are simulated by pressurized spray and condensation systems while damaging effects of sunlight are simulated by fluorescent UV lamps. The exposure temperature is automatically controlled. Cyclical weather conditions can also be simulated. Three types of fluorescent lamps are commonly used for QUV. Two of these are of the type UVB (medium wavelength UV), while the third is UVA (longer wavelength UV similar to black light). All these lamps produce mostly UV as opposed to visible or infrared light. The lamp used, and therefore the wavelength of UV light produced will affect how realistic the final degradation results will be. In reality, natural sunlight contains radiation from many areas of the spectrum. This includes both UVA and UVB, however the UVB radiation is at the lowest end of natural light and is less predominant than UVA. Since it has a shorter wavelength, it also has a higher energy. This makes UVB more damaging not only because it increase chemical reaction kinetics, but also because it can initiate chemical reactions to occur which would not normally be possible under natural condition. For this reason, testing using only UVB lamps have been shown to have poor correlation relative to natural weather testing of the same samples.

SEPAP



A view of a SEPAP weather tester

The SEPAP 12-24 fr:Photovieillissement accéléré en SEPAP has been designed, in the late seventies, by the scientists of University Blaise Pascal , specialists of molecular photochemistry, to provoke in accelerated controlled conditions the same chemical evolutions as those occurring at long term under the permanent physicochemical stresses of the environment, i.e. UV - heat – atmospheric oxygen and water as an aggravating agent.

That ageing chamber based on fundamental concepts differs widely from the ageing units based on the simulation of environmental stresses in non-accelerated conditions like in some xenon based instruments. In SEPAP 12-24 :

- the samples are rotating to insure an homogenous exposure ;
- the incident light is supplied by four medium-pressure Mercury-vapor lamps filtered by the borosilicate envelops of the lamps ; the incident light is not containing any radiations whose wavelength would be shorter than 300 nm. Although the spectral distribution is not simulating the solar light, the vibrational relaxations which occur from each excited states insure the absence of any wavelength effect under the mercury arc excitation, the light spectral distribution influencing only the rate of the photoreactions. That concept has been largely checked in the last 30 years ;
- since the photochemical activation (due to UV) and the thermal excitation cannot be deconjugated, it is essential to control the temperature of the samples surfaces directly exposed to light. A patented device insures that requirement in SEPAP 12-24 ;
- the water present in the polymeric blend exposed in SEPAP 12-24 is formed through the decomposition of the primary hydroperoxides ; no external water is

brought on the exposed sample. The water effect on artificial ageing is handled either in SEPAP 12-24 H (when conjugated with the effects of UV, heat and oxygen), or through post-photochemical immersions in neutral water (in absence of conjugated effects') .

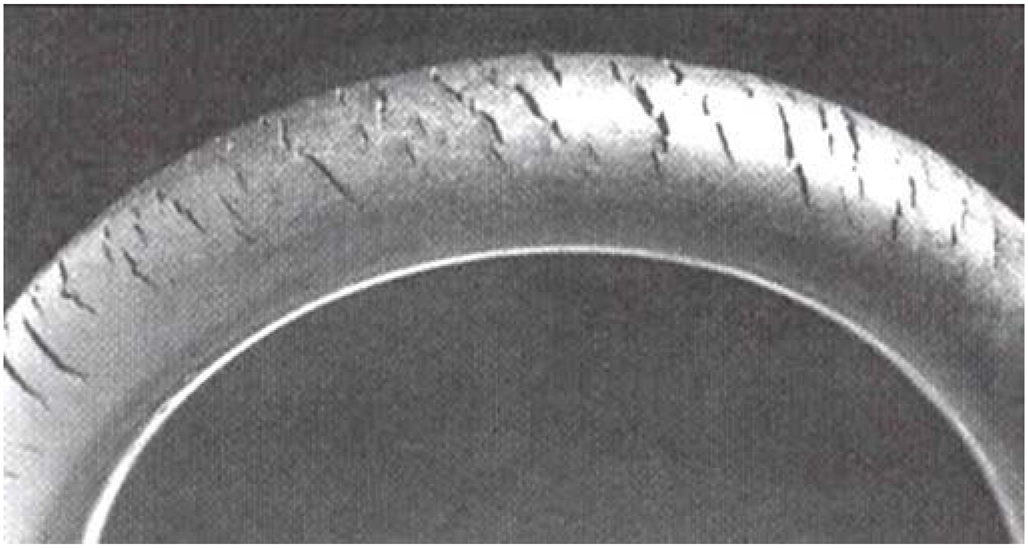
The durability control of polymeric formulations through the SEPAP 12-24 testing is currently required by some French and European standards and by many industrial companies

The (French) National Center for Photoprotection Assessment (CNEP) is currently using SEPAP for industrial applications and is more generally involved in polymer and polymer failures analysis (National Centre for the Evaluation of Photoprotection) for plastic industries.

Chapter 12

Ozone Cracking and Fracture Mechanics

Ozone cracking



Ozone cracking in natural rubber tubing

Cracks can be formed in many different elastomers by ozone attack, and the characteristic form of attack of vulnerable rubbers is known as **ozone cracking**. The problem was formerly very common, especially in tires, but is now rarely seen in those products owing to preventive measures.

However, it does occur in many other safety-critical items such as fuel lines and rubber seals, such as gaskets and O-rings, where ozone attack is considered unlikely. Only a trace amount of the gas is needed to initiate cracking, and so these items can also succumb to the problem.

Susceptible elastomers

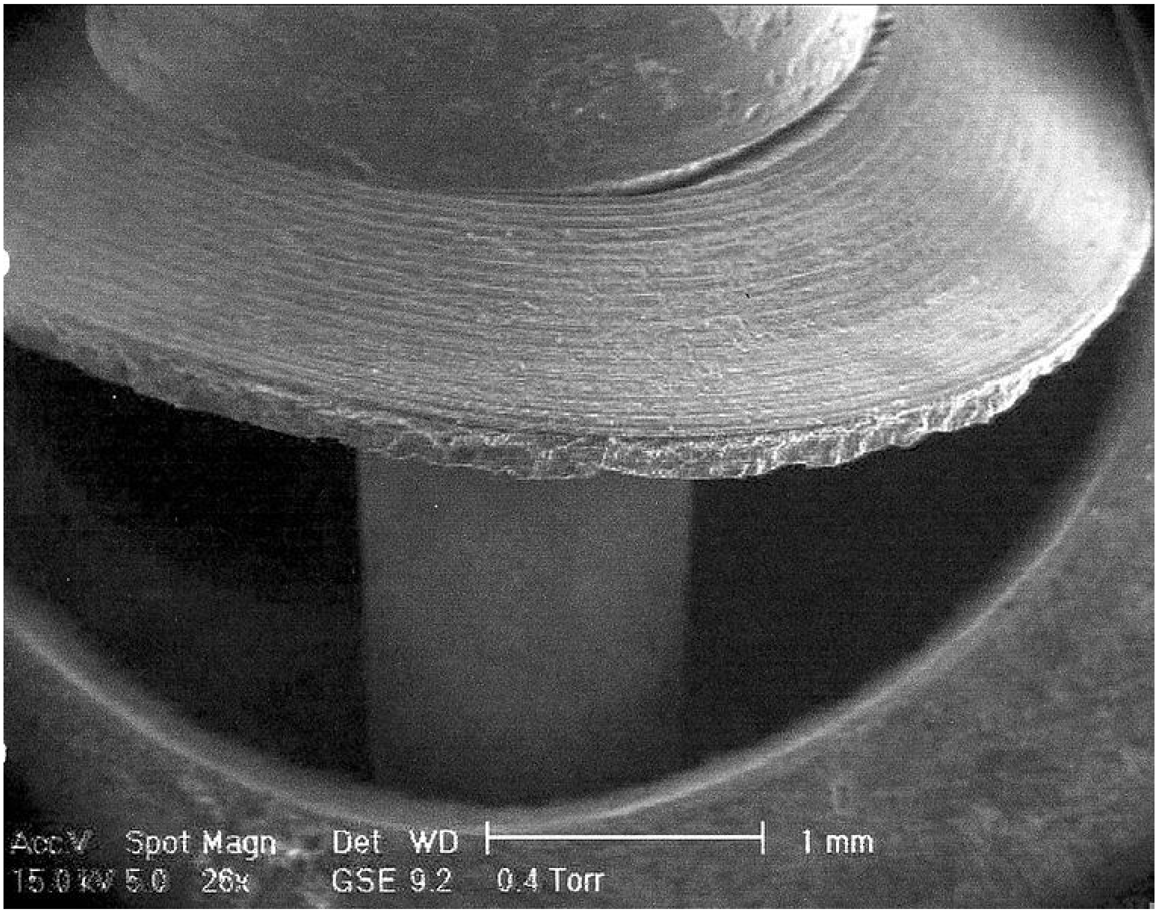
Tiny traces of ozone in the air will attack double bonds in rubber chains, with natural rubber, polybutadiene, styrene-butadiene rubber and nitrile rubber being most sensitive to degradation. Every repeat unit in the first three materials has a double bond, so every unit can be degraded by ozone. Nitrile rubber is a copolymer of butadiene and acrylonitrile units, but the proportion of acrylonitrile is usually lower than butadiene, so attack occurs. Butyl rubber is more resistant but still has a small number of double bonds in its chains, so attack is possible. Exposed surfaces are attacked first, the density of cracks varying with ozone gas concentration. The higher the concentration, the greater the number of cracks formed.

Ozone-resistant elastomers include EPDM, fluoroelastomers like Viton and polychloroprene rubbers like Neoprene. Attack is less likely because double bonds form a very small proportion of the chains, and with the latter, the chlorination reduces the electron density in the double bonds, therefore lowering their propensity to react with ozone. Silicone rubber, Hypalon and polyurethanes are also ozone-resistant.

Form of cracking

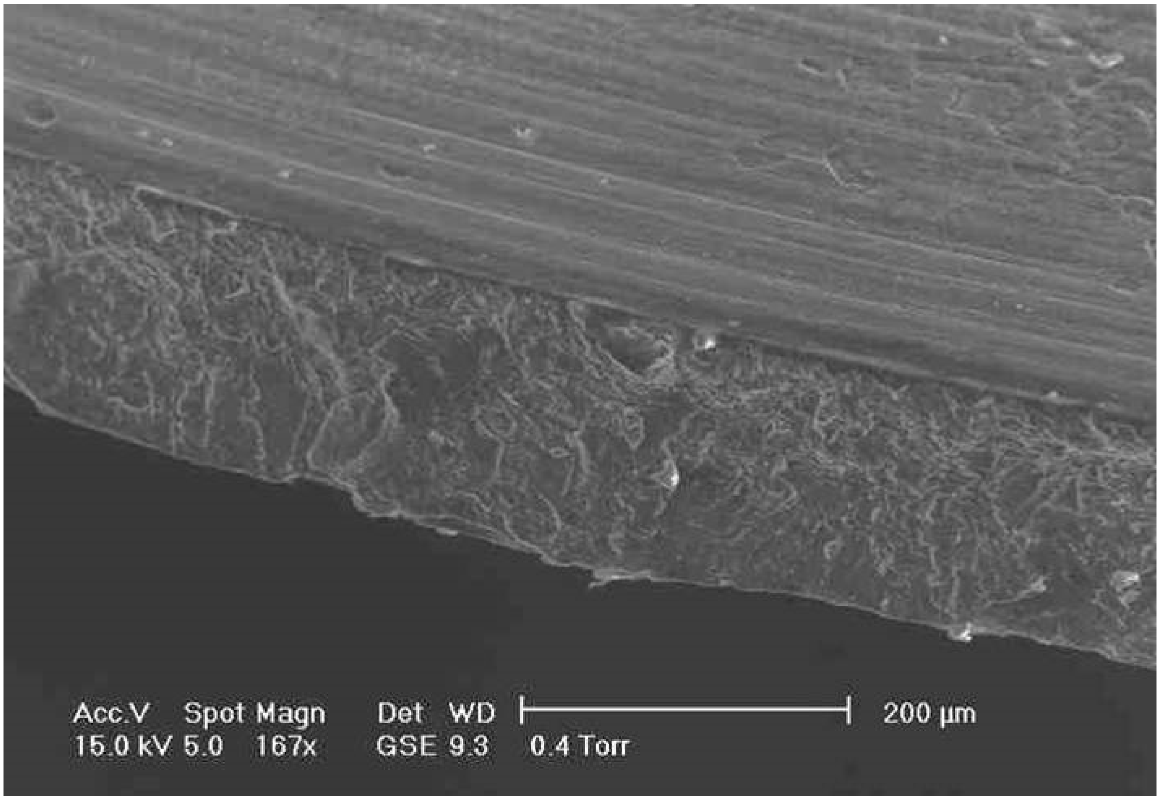
Macrophotograph of ozone cracking in NBR (Nitrile Butadiene Rubber) diaphragm seal

Ozone cracks form in products under tension, but the critical strain is very small. The cracks are always oriented at right angles to the strain axis, so will form around the circumference in a rubber tube bent over. Such cracks are very dangerous when they occur in fuel pipes because the cracks will grow from the outside exposed surfaces into the bore of the pipe, so fuel leakage and fire may follow. Seals are also susceptible to attack, such as diaphragm seals in air lines. Such seals are often critical for the operation of pneumatic controls, and if a crack penetrates the seal, all functions of the system can be lost. Nitrile rubber seals are commonly used in pneumatic systems because of its oil resistance. However, if ozone gas is present, cracking will occur in the seals unless preventative measures are taken.



environmental scanning electron microscope image of ozone cracks in NBR diaphragm seal formed at sharp corners in seal

Ozone attack will occur at the most sensitive zones in a seal, especially sharp corners where the strain is greatest when the seal is flexing in use. The corners represent stress concentrations, so the tension is at a maximum when the diaphragm of the seal is bent under air pressure.

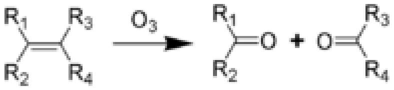


Close-up of ozone crack (using ESEM) in NBR diaphragm seal

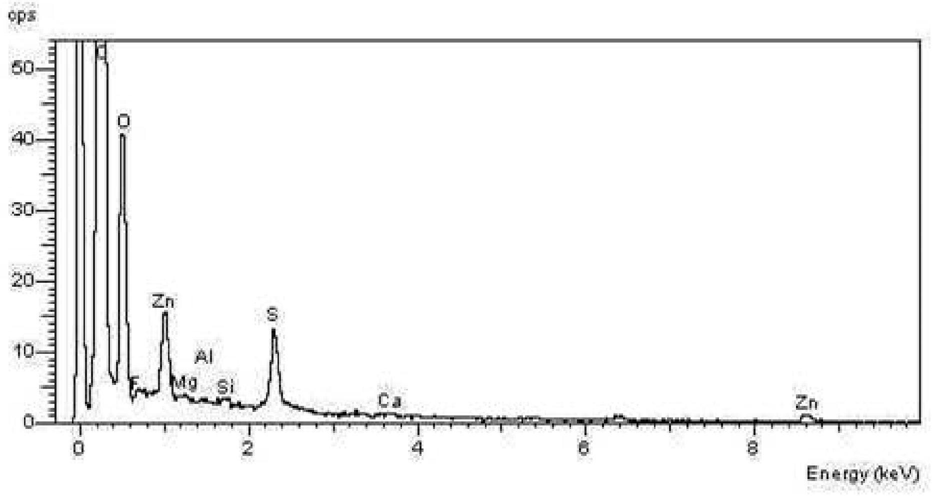
The seal shown at left failed from traces of ozone at circa 1 ppm, and once cracking had started, it continued as long as the gas was present. This particular failure led to loss of production on a semi-conductor fabrication line. The problem was solved by adding effective filters in the air line and by modifying the design to eliminate the very sharp corners. An ozone-resistant elastomer such as Viton was also considered as a replacement for the Nitrile rubber. The pictures were taken using ESEM for maximum resolution.

Ozonolysis

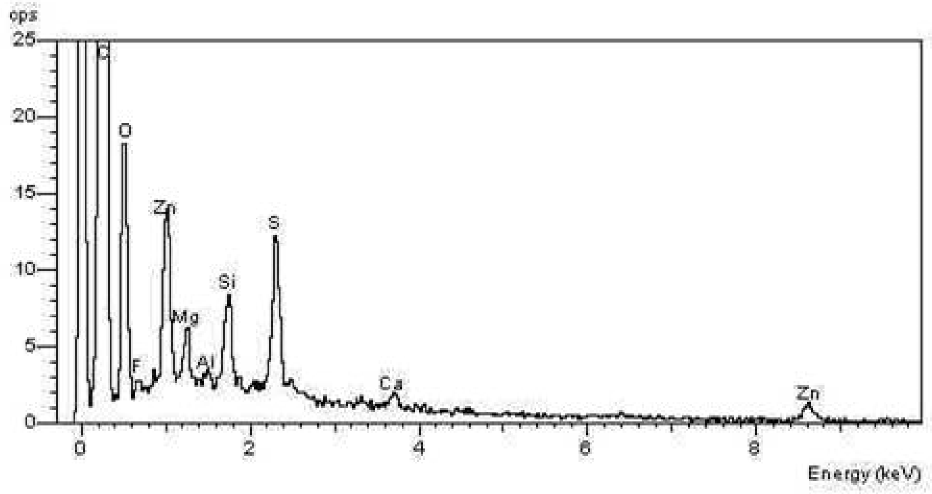
The reaction occurring between double bonds and ozone is known as ozonolysis when one molecule of the gas reacts with the double bond:



The immediate result is formation of an ozonide, which then decomposes rapidly so that the double bond is cleaved. This is the critical step in chain breakage when polymers are attacked. The strength of polymers depends on the chain molecular weight or degree of polymerization, the higher the chain length, the greater the mechanical strength (such as tensile strength). By cleaving the chain, the molecular weight drops rapidly and there comes a point when it has little strength whatsoever, and a crack forms. Further attack occurs in the freshly exposed crack surfaces and the crack grows steadily until it completes a circuit and the product separates or fails. In the case of a seal or a tube, failure occurs when the wall of the device is penetrated.



EDX spectrum of crack surface



EDX spectrum of unaffected rubber surface

The carbonyl end groups which are formed are usually aldehydes or ketones, which can oxidise further to carboxylic acids. The net result is a high concentration of elemental oxygen on the crack surfaces, which can be detected using Energy-dispersive X-ray spectroscopy in the environmental SEM, or ESEM. The spectrum at left shows the high oxygen peak compared with a constant sulfur peak. The spectrum at right shows the unaffected elastomer surface spectrum, with a relatively low oxygen peak compared with the sulfur peak.

Prevention

The problem can be prevented by adding antiozonants to the rubber before vulcanization. Ozone cracks were commonly seen in automobile tire sidewalls, but are now seen rarely thanks to the use of these additives. A common and low cost antiozonant is a wax which bleeds to the surface and forms a protective layer, but other specialist chemicals are also widely used.

On the other hand, the problem does recur in unprotected products such as rubber tubing and seals, where ozone attack is thought to be impossible. Unfortunately, traces of ozone can turn up in the most unexpected situations. Using ozone-resistant rubbers is another way of inhibiting cracking.

For high value equipment where loss of function can cause serious problems, low cost seals may be replaced at frequent intervals so as to preclude failure.

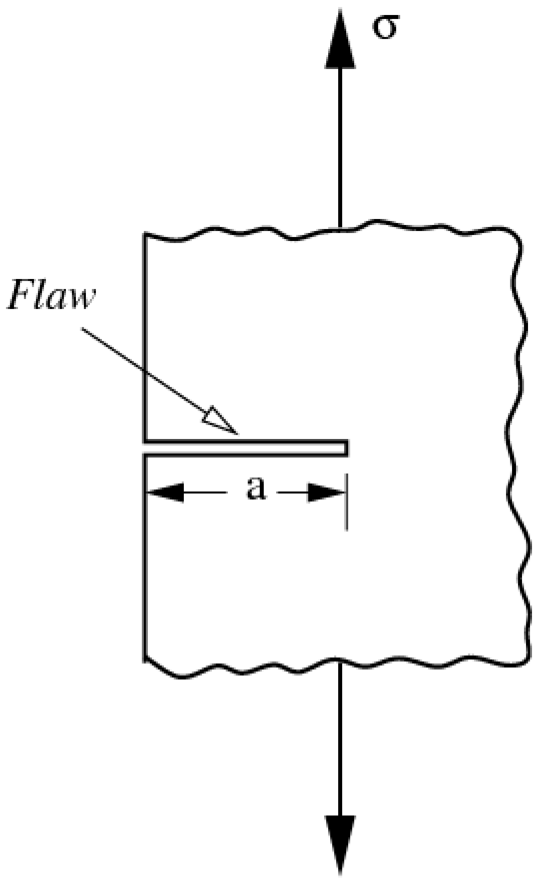
Ozone gas is produced during electric discharge by sparking or corona discharge for example. Static electricity can build up within machines like compressors with moving parts constructed from insulating materials. If those compressors feed pressurised air into a closed pneumatic system, then all seals in the system may be at risk from ozone cracking.

Ozone is also produced by the action of sunlight on volatile organic liquids or VOLs, such as gasoline vapour present in the air of towns and cities, in a problem known as photochemical smog. The ozone formed can drift many miles before it is destroyed by further reactions.

Fracture mechanics

Fracture mechanics is the field of mechanics concerned with the study of the propagation of cracks in materials. It uses methods of analytical solid mechanics to calculate the driving force on a crack and those of experimental solid mechanics to characterize the material's resistance to fracture.

In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components. It applies the physics of stress and strain, in particular the theories of elasticity and plasticity, to the microscopic crystallographic defects found in real materials in order to predict the macroscopic mechanical failure of bodies. Fractography is widely used with fracture mechanics to understand the causes of failures and also verify the theoretical failure predictions with real life failures.



An edge crack (flaw) of length *a* in a material.

Linear elastic fracture mechanics

Griffith's criterion

Fracture mechanics was developed during World War I by English aeronautical engineer, A. A. Griffith, to explain the failure of brittle materials. Griffith's work was motivated by two contradictory facts:

- The stress needed to fracture bulk glass is around 100 MPa (15,000 psi).
- The theoretical stress needed for breaking atomic bonds is approximately 10,000 MPa (1,500,000 psi).

A theory was needed to reconcile these conflicting observations. Also, experiments on glass fibers that Griffith himself conducted suggested that the fracture stress increases as the fiber diameter decreases. Hence the uniaxial tensile strength, which had been used extensively to predict material failure before Griffith, could not be a specimen-independent material property. Griffith suggested that the low fracture strength observed in experiments, as well as the size-dependence of strength, was due to the presence of microscopic flaws in the bulk material.

To verify the flaw hypothesis, Griffith introduced an artificial flaw in his experimental specimens. The artificial flaw was in the form of a surface crack which was much larger than other flaws in a specimen. The experiments showed that the product of the square root of the flaw length (a) and the stress at fracture (σ_f) was nearly constant, which is expressed by the equation:

$$\sigma_f \sqrt{a} \approx C$$

An explanation of this relation in terms of linear elasticity theory is problematic. Linear elasticity theory predicts that stress (and hence the strain) at the tip of a sharp flaw in a linear elastic material is infinite. To avoid that problem, Griffith developed a thermodynamic approach to explain the relation that he observed.

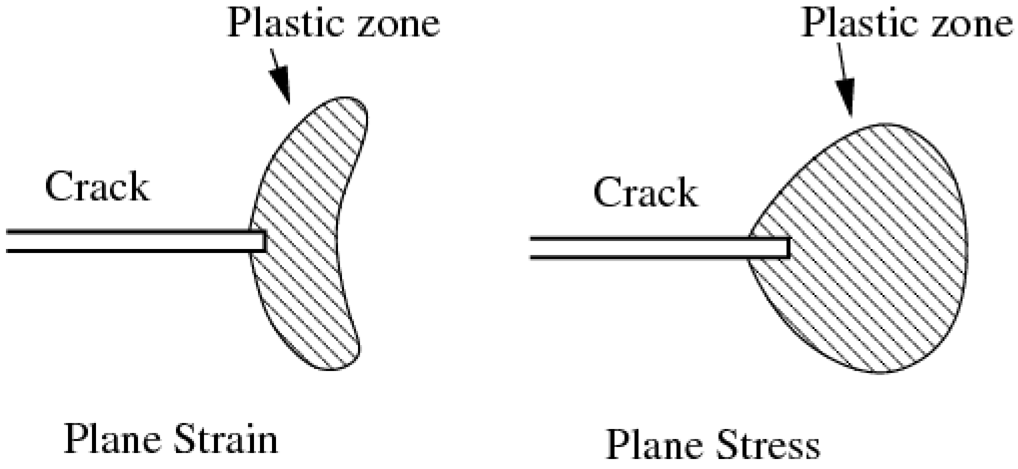
The growth of a crack requires the creation of two new surfaces and hence an increase in the surface energy. Griffith found an expression for the constant C in terms of the surface energy of the crack by solving the elasticity problem of a finite crack in an elastic plate. Briefly, the approach was:

- Compute the potential energy stored in a perfect specimen under an uniaxial tensile load.
- Fix the boundary so that the applied load does no work and then introduce a crack into the specimen. The crack relaxes the stress and hence reduces the elastic energy near the crack faces. On the other hand, the crack increases the total surface energy of the specimen.
- Compute the change in the free energy (surface energy − elastic energy) as a function of the crack length. Failure occurs when the free energy attains a peak value at a critical crack length, beyond which the free energy decreases by increasing the crack length, i.e. by causing fracture. Using this procedure, Griffith found that

$$C = \sqrt{\frac{2E\gamma}{\pi}}$$

where E is the Young's modulus of the material and γ is the surface energy density of the material. Assuming E = 62 GPa and γ = 1 J/m^2 gives excellent agreement of Griffith's predicted fracture stress with experimental results for glass.

Irwin's modification



The plastic zone around a crack tip in a ductile material.

Griffith's work was largely ignored by the engineering community until the early 1950s. The reasons for this appear to be (a) in the actual structural materials the level of energy needed to cause fracture is orders of magnitude higher than the corresponding surface energy, and (b) in structural materials there are always some inelastic deformations around the crack front that would make the assumption of linear elastic medium with infinite stresses at the crack tip highly unrealistic. **F. Erdogan (2000)**

Griffith's theory provides excellent agreement with experimental data for brittle materials such as glass. For ductile materials such as steel, though the relation $\sigma_y\sqrt{a} = C$ still holds, the surface energy (γ) predicted by Griffith's theory is usually unrealistically high. A group working under G. R. Irwin at the U.S. Naval Research Laboratory (NRL) during World War II realized that plasticity must play a significant role in the fracture of ductile materials.

In ductile materials (and even in materials that appear to be brittle), a plastic zone develops at the tip of the crack. As the applied load increases, the plastic zone increases in size until the crack grows and the material behind the crack tip unloads. The plastic loading and unloading cycle near the crack tip leads to the dissipation of energy as heat. Hence, a dissipative term has to be added to the energy balance relation devised by Griffith for brittle materials. In physical terms, additional energy is needed for crack growth in ductile materials when compared to brittle materials.

Irwin's strategy was to partition the energy into two parts:

- the stored elastic strain energy which is released as a crack grows. This is the thermodynamic driving force for fracture.
- the dissipated energy which includes plastic dissipation and the surface energy (and any other dissipative forces that may be at work). The dissipated energy

provides the thermodynamic resistance to fracture. Then the total energy dissipated is

$$G = 2\gamma + G_p$$

where γ is the surface energy and G_p is the plastic dissipation (and dissipation from other sources) per unit area of crack growth.

The modified version of Griffith's energy criterion can then be written as

$$\sigma_f \sqrt{a} = \sqrt{\frac{E\ G}{\pi}}.$$

For brittle materials such as glass, the surface energy term dominates and $G \approx 2\gamma = 2\ J/m^2$. For ductile materials such as steel, the plastic dissipation term dominates and $G \approx G_p = 1000\ J/m^2$. For polymers close to the glass transition temperature, we have intermediate values of $G \approx 2 - 1000\ J/m^2$.

Stress intensity factor

Another significant achievement of Irwin and his colleagues was to find a method of calculating the amount of energy available for fracture in terms of the asymptotic stress and displacement fields around a crack front in a linear elastic solid. This asymptotic expression for the stress field around a crack tip is

$$\sigma_{ij} \approx \left(\frac{K}{\sqrt{2\pi r}}\right)\ f_{ij}(\theta)$$

where σ_{ij} are the Cauchy stresses, r is the distance from the crack tip, θ is the angle with respect to the plane of the crack, and f_{ij} are functions that are independent of the crack geometry and loading conditions. Irwin called the quantity K the *stress intensity factor*. Since the quantity f_{ij} is dimensionless, the stress intensity factor can be expressed in units of $\mathrm{MPa}\text{-}\sqrt{\mathrm{m}}$.

When a rigid line inclusion is considered, a similar asymptotic expression for the stress fields is obtained.

Strain energy release

Irwin was the first to observe that if the size of the plastic zone around a crack is small compared to the size of the crack, the energy required to grow the crack will not be critically dependent on the state of stress at the crack tip. In other words, a purely elastic solution may be used to calculate the amount of energy available for fracture.

The energy release rate for crack growth or *strain energy release rate* may then be calculated as the change in elastic strain energy per unit area of crack growth, i.e.,

$$G := -\left[\frac{\partial U}{\partial a}\right]_P = -\left[\frac{\partial U}{\partial a}\right]_u$$

where U is the elastic energy of the system and a is the crack length. Either the load P or the displacement u can be kept fixed while evaluating the above expressions.

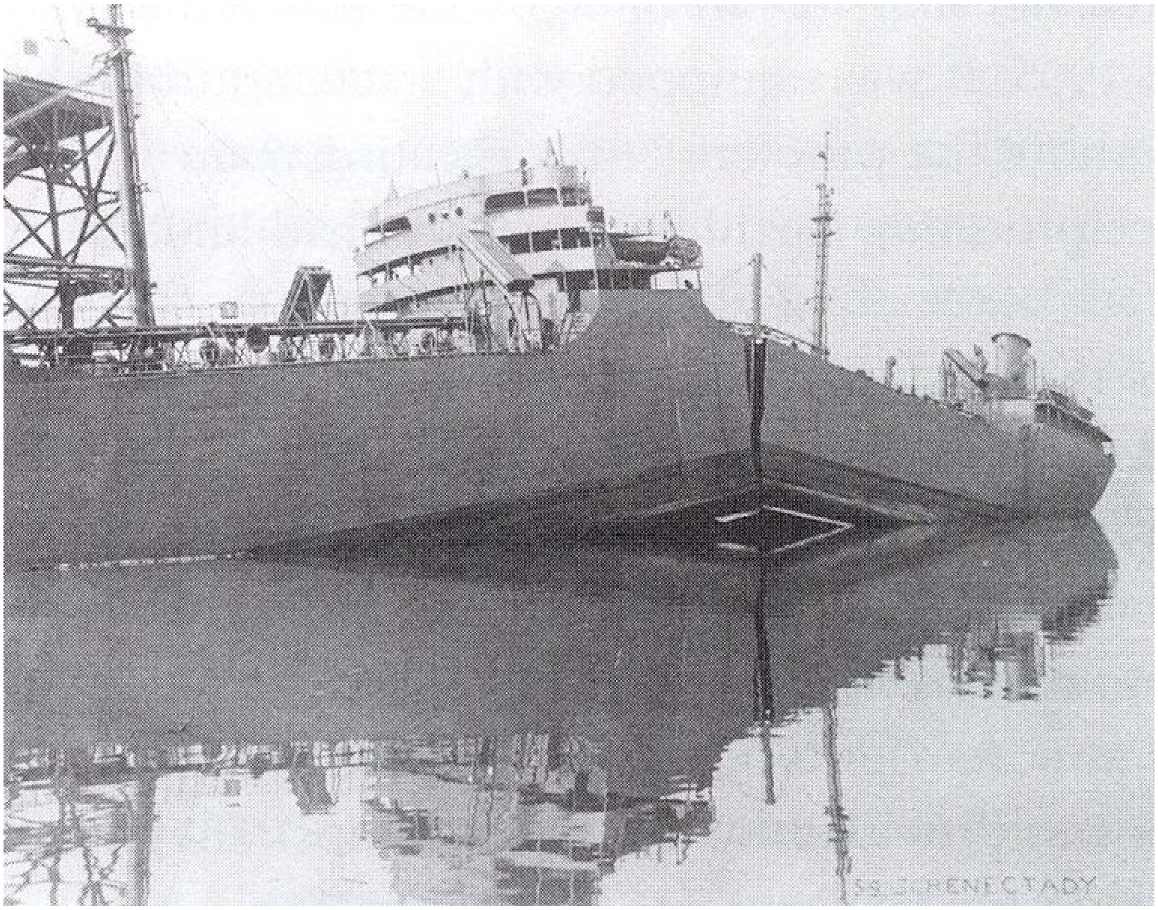
Irwin showed that for a mode I crack (opening mode) the strain energy release rate and the stress intensity factor are related by:

$$G = G_I = \begin{cases} \dfrac{K_I^2}{E} & \text{plane stress} \\ \dfrac{(1-\nu^2)K_I^2}{E} & \text{plane strain} \end{cases}$$

where E is the Young's modulus, v is Poisson's ratio, and K_{I} is the stress intensity factor in mode I. Irwin also showed that the strain energy release rate of a planar crack in a linear elastic body can be expressed in terms of the mode I, mode II (sliding mode), and mode III (tearing mode) stress intensity factors for the most general loading conditions.

Next, Irwin adopted the additional assumption that the size and shape of the energy dissipation zone remains approximately constant during brittle fracture. This assumption suggests that the energy needed to create a unit fracture surface is a constant that depends only on the material. This new material property was given the name *fracture toughness* and designated G_{Ic}. Today, it is the critical stress intensity factor K_{Ic} which is accepted as the defining property in linear elastic fracture mechanics.

Limitations



The S.S. *Schenectady* split apart by brittle fracture while in harbor (1944)

But a problem arose for the NRL researchers because naval materials, e.g., ship-plate steel, are not perfectly elastic but undergo significant plastic deformation at the tip of a crack. One basic assumption in Irwin's linear elastic fracture mechanics is that the size of the plastic zone is small compared to the crack length. However, this assumption is quite restrictive for certain types of failure in structural steels though such steels can be prone to brittle fracture, which has led to a number of catastrophic failures.

Linear-elastic fracture mechanics is of limited practical use for structural steels for another more practical reason. Fracture toughness testing is very expensive and engineers believe that sufficient information for selection of steels can be obtained from the simpler and cheaper Charpy impact test.

Nonlinear elasticity and plasticity

Vertical stabilizer, which separated from American Airlines Flight 587, leading to a fatal crash

Most engineering materials show some nonlinear elastic and inelastic behavior under operating conditions that involve large loads. In such materials the assumptions of linear elastic fracture mechanics may not hold, that is,

- the plastic zone at a crack tip may have a size of the same order of magnitude as the crack size
- the size and shape of the plastic zone may change as the applied load is increased and also as the crack length increases.

Therefore a more general theory of crack growth is needed for elastic-plastic materials that can account for:

- the local conditions for initial crack growth which include the nucleation, growth, and coalescence of voids or decohesion at a crack tip.
- a global energy balance criterion for further crack growth and unstable fracture.

R-curve

An early attempt in the direction of elastic-plastic fracture mechanics was Irwin's **crack extension resistance curve** or **R-curve**. This curve acknowledges the fact that the resistance to fracture increases with growing crack size in elastic-plastic materials. The

R-curve is a plot of the total energy dissipation rate as a function of the crack size and can be used to examine the processes of slow stable crack growth and unstable fracture. However, the R-curve was not widely used in applications until the early 1970s. The main reasons appear to be that the R-curve depends on the geometry of the specimen and the crack driving force may be difficult to calculate.

J-integral

In the mid-1960s James R. Rice (then at Brown University) and G. P. Cherepanov independently developed a new toughness measure to describe the case where there is sufficient crack-tip deformation that the part no longer obeys the linear-elastic approximation. Rice's analysis, which assumes non-linear elastic (or monotonic deformation-theory plastic) deformation ahead of the crack tip, is designated the J integral. This analysis is limited to situations where plastic deformation at the crack tip does not extend to the furthest edge of the loaded part. It also demands that the assumed non-linear elastic behavior of the material is a reasonable approximation in shape and magnitude to the real material's load response.

Fully plastic failure

If the material is so tough that the yielded region ahead of the crack extends to the far edge of the specimen before fracture, the crack is no longer an effective stress concentrator. Instead, the presence of the crack merely serves to reduce the load-bearing area. In this regime the failure stress is conventionally assumed to be the average of the yield and ultimate strengths of the material.

Engineering applications

The following information is needed for a fracture mechanics prediction of failure:

- Applied load
- Residual stress
- Size and shape of the part
- Size, shape, location, and orientation of the crack

Usually not all of this information is available and conservative assumptions have to be made.

Occasionally post-mortem fracture-mechanics analyses are carried out. In the absence of an extreme overload, the causes are either insufficient toughness (K_{Ic}) or an excessively large crack that was not detected during routine inspection.

Short summary

Arising from the manufacturing process, interior and surface flaws are found in all metal structures. Not all such flaws are unstable under service conditions. Fracture mechanics is the analysis of flaws to discover those that are safe (that is, do not grow) and those that are liable to propagate as cracks and so cause failure of the flawed structure. Ensuring safe operation of structure despite these inherent flaws is achieved through damage tolerance analysis. Fracture mechanics as a subject for critical study has barely been around for a century and thus is relatively new. There is a high demand for engineers with fracture mechanics expertise—particularly in this day and age where engineering failure is considered 'shocking' amongst the general public.

Appendix: mathematical relations

Griffith's criterion

For the simple case of a thin rectangular plate with a crack perpendicular to the load Griffith's theory becomes:

$$G = \frac{\pi \sigma^2 a}{E} \qquad (1.1)$$

where *G* is the strain energy release rate, σ is the applied stress, *a* is half the crack length, and *E* is the Young's modulus. The strain energy release rate can otherwise be understood as: *the rate at which energy is absorbed by growth of the crack.*

However, we also have that:

$$G_c = \frac{\pi \sigma_f^2 a}{E} \qquad (1.2)$$

If $G \geq G_c$, this is the criterion for which the crack will begin to propagate.

Irwin's modifications

Eventually a modification of Griffith's solids theory emerged from this work; a term called stress intensity replaced strain energy release rate and a term called fracture toughness replaced surface weakness energy. Both of these terms are simply related to the energy terms that Griffith used:

$$K_I = \sigma \sqrt{\pi a} \qquad (2.1)$$

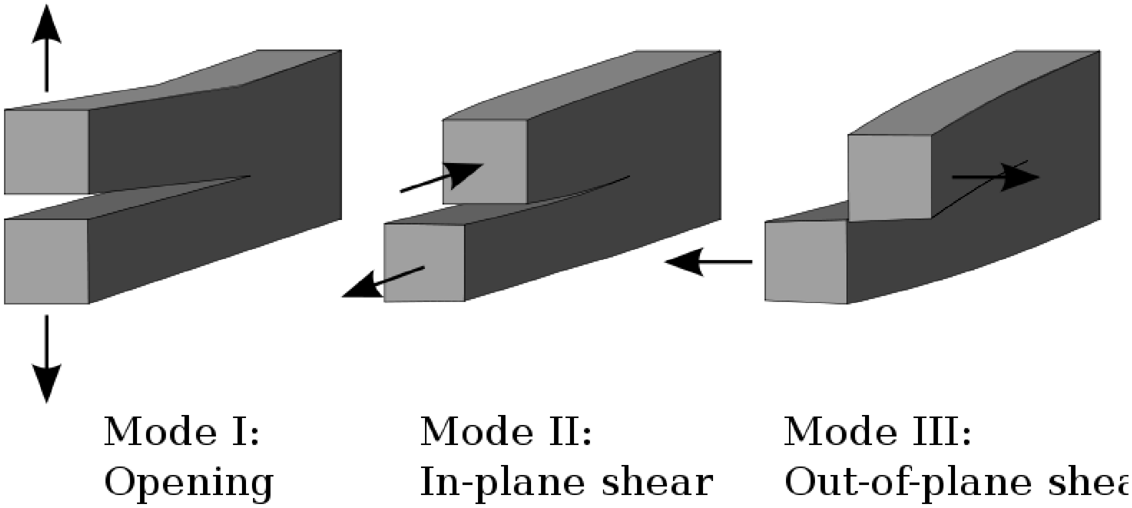
and

$$K_c = \sqrt{E G_c} \text{ (for plane stress)} \qquad (2.2)$$

$$K_c = \sqrt{\frac{E G_c}{1 - \nu^2}} \text{ (for plane strain)} \qquad (2.3)$$

where K_I is the stress intensity, K_c the fracture toughness, and ν is Poisson's ratio. It is important to recognize the fact that fracture parameter K_c has different values when measured under plane stress and plane strain

Fracture occurs when $K_I \geq K_c$. For the special case of plane strain deformation, K_c becomes K_{Ic} and is considered a material property. The subscript I arises because of the different ways of loading a material to enable a crack to propagate. It refers to so-called "mode I" loading as opposed to mode II or III:



The three fracture modes.

There are three ways of applying a force to enable a crack to propagate:

- **Mode I crack** – Opening mode (a tensile stress normal to the plane of the crack)
- **Mode II crack** – Sliding mode (a shear stress acting parallel to the plane of the crack and perpendicular to the crack front)
- **Mode III crack** – Tearing mode (a shear stress acting parallel to the plane of the crack and parallel to the crack front)

We must note that the expression for K_I in equation 2.1 will be different for geometries other than the center-cracked infinite plate, as discussed in stress intensity. Consequently, it is necessary to introduce a dimensionless correction factor, Y, in order to characterize the geometry. We thus have:

$$K_I = Y\sigma\sqrt{\pi a} \qquad (2.4)$$

where Y is a function of the crack length and width of sheet given by:

$$Y\left(\frac{a}{W}\right) = \sqrt{\sec\left(\frac{\pi a}{W}\right)} \qquad (2.5)$$

for a sheet of finite width *W* containing a through-thickness crack of length 2*a*, or

$$Y\left(\frac{a}{W}\right) = 1.12 - \frac{0.41}{\sqrt{\pi}}\frac{a}{W} + \frac{18.7}{\sqrt{\pi}}\left(\frac{a}{W}\right)^2 - \cdots \qquad (2.6)$$

for a sheet of finite width *W* containing a through-thickness edge crack of length *a*

Elasticity and plasticity

Since engineers became accustomed to using K_{Ic} to characterise fracture toughness, a relation has been used to reduce J_{Ic} to it:

$K_{Ic} = \sqrt{E^* J_{Ic}}$ where $E^* = E$ for plane stress and $E^* = \frac{E}{1-\nu^2}$ for plane strain (3.1)

The remainder of the mathematics employed in this approach is interesting, but is probably better summarised in external pages due to its complex nature.

Chapter 13

Failure Theory (Material)

Failure theory is the science of predicting the conditions under which solid materials lose their strength under the action of external loads. The failure of a material is usually classified into brittle failure (fracture) or ductile failure (yield). Depending on the conditions (such as temperature, state of stress, loading rate) most materials can fail in a brittle or ductile manner or both. However, for most practical situations, a material may be classified as either brittle or ductile. Though failure theory has been in development for over 200 years, its level of acceptability is yet to reach that of continuum mechanics.

In mathematical terms, failure theory is expressed in the form of various failure criteria which are valid for specific materials. Failure criteria are functions in stress or strain space which separate "failed" states from "unfailed" states. A precise physical definition of a "failed" state is not easily quantified and several working definitions are in use in the engineering community. Quite often, phenomenological failure criteria of the same form are used to predict brittle failure and ductile yield.

Material failure

In materials science, **material failure** is the loss of load carrying capacity of a material unit. This definition *per se* introduces the fact that material failure can be examined in different scales, from microscopic, to macroscopic. In structural problems, where the structural response may be beyond the initiation of nonlinear material behaviour, material failure is of profound importance for the determination of the integrity of the structure. On the other hand, due to the lack of globally accepted fracture criteria, the determination of the structure's damage, due to material failure, is still under intensive research.

Types of material failure

Material failure can be distinguished in two broader categories depending on the scale in which the material is examined:

Microscopic failure

Microscopic material failure is defined in terms of crack propagation and initiation. Such methodologies are useful for gaining insight in the cracking of specimens and simple structures under well defined global load distributions. Microscopic failure considers the initiation and propagation of a crack. Failure criteria in this case are related to microscopic fracture. Some of the most popular failure models in this area are the micromechanical failure models, which combine the advantages of continuum mechanics and classical fracture mechanics. Such models are based on the concept that during plastic deformation, microvoids nucleate and grow until a local plastic neck or fracture of the intervoid matrix occurs, which causes the coalescence of neighbouring voids. Such a model, proposed by Gurson and extended by Tvergaard and Needleman, is known as GTN. Another approach, proposed by Rousselier, is based on continuum damage mechanics (CDM) and thermodynamics. Both models form a modification of the von Mises yield potential by introducing a scalar damage quantity, which represents the void volume fraction of cavities, the porosity f.

Macroscopic failure

Macroscopic material failure is defined in terms of load carrying capacity or energy storage capacity, equivalently. Li presents a classification of macroscopic failure criteria in four categories:

- Stress or strain failure
- Energy type failure (S-criterion, T-criterion)
- Damage failure
- Empirical failure.

Five general levels are considered, at which the meaning of deformation and failure is interpreted differently: the structural element scale, the macroscopic scale where macroscopic stress and strain are defined, the mesoscale which is represented by a typical void, the microscale and the atomic scale. The material behaviour at one level is considered as a collective of its behaviour at a sublevel. An efficient deformation and failure model should be consistent at every level.

Brittle material failure criteria

Failure of brittle materials can be determined using several approaches:

- Phenomenological failure criteria
- Linear elastic fracture mechanics

- elastic-plastic fracture mechanics
- Energy-based methods
- Cohesive zone methods

Phenomenological failure criteria

The failure criteria that were developed for brittle solids were the maximum stress/strain criteria. The **maximum stress criterion** assumes that a material fails when the maximum principal stress σ_1 in a material element exceeds the uniaxial tensile strength of the material. Alternatively, the material will fail if the minimum principal stress σ_3 is less than the uniaxial compressive strength of the material. If the uniaxial tensile strength of the material is σ_t and the uniaxial compressive strength is σ_c, then the safe region for the material is assumed to be

$$\sigma_c < \sigma_3 < \sigma_1 < \sigma_t$$

Note that the convention that tension is positive has been used in the above expression.

The **maximum strain criterion** has a similar form except that the principal strains are compared with experimentall determined uniaxial strains at failure, i.e.,

$$\varepsilon_c < \varepsilon_3 < \varepsilon_1 < \varepsilon_t$$

The maximum principal stress and strain criteria continue to be widely used in spite of severe shortcomings.

Numerous other phenomenological failure criteria can be found in the engineering literature. The degree of success of these criteria in predicting failure has been limited. For brittle materials, some popular failure criteria are

- criteria based on invariants of the Cauchy stress tensor
- the Tresca or maximum shear stress failure criterion
- the von Mises or maximum elastic distortional energy criterion
- the Mohr-Coulomb failure criterion for cohesive-frictional solids
- the Drucker-Prager failure criterion for pressure-dependent solids
- the Bresler-Pister failure criterion for concrete
- the Willam-Warnke failure criterion for concrete
- the Hankinson criterion, an empirical failure criterion that is used for orthotropic materials such as wood.
- the Hill yield criteria for anisotropic solids
- the Tsai-Wu failure criterion for anisotropic composites
- the Johnson-Holmquist damage model for high-rate deformations of isotropic solids
- the Hoek-Brown failure criterion for rock masses

Linear elastic fracture mechanics

The approach taken in linear elastic fracture mechanics is to estimate the amount of energy needed to grow a preexisting crack in a brittle material. The earliest fracture mechanics approach for unstable crack growth is Griffiths' theory . When applied to the mode I opening of a crack, Griffiths' theory predicts that the critical stress (σ) needed to propagate the crack is given by

$$\sigma = \sqrt{\frac{2E\gamma}{\pi\ a}}$$

where E is the Young's modulus of the material, γ is the surface energy per unit area of the crack, and $2a$ is the crack length. The quantity $\sigma\sqrt{\pi a}$is postulated as a material parameter called the '*fracture toughness*. The mode I fracture toughness is defined as

$$K_{Ic} = \sigma_c\sqrt{\pi a}$$

and is determined experimentally. Similar quantities K_{IIc} and K_{IIIc} can be determined for mode II and model III loading conditions.

The state of stress around cracks of various shapes can be expressed in terms of their stress intensity factors. Linear elastic fracture mechanics predicts that a crack will extend when the stress intensity factor at the crack tip is greater than the fracture toughness of the material. Therefore the critical applied stress can also be determined once the stress intensity factor at a crack tip is known.

Energy-based methods

The linear elastic fracture mechanics method is difficult to apply for anisotropic materials (such as composites) or for situations where the loading or the geometry are complex. The **strain energy release rate** approach has proved quite useful for such situations. The strain energy release rate for a mode I crack which runs through the thickness of a plate is defined as

$$G_I := \frac{P}{2t}\,\frac{du}{da}$$

where P is the applied load, t is the thickness of the plate, u is the displacement at the point of application of the load due to crack growth, and $2a$ is the length of the crack. The crack is expected to propagate when the strain energy release rate exceeds a critical value G_{Ic} - called the **critical strain energy release rate**.

The fracture toughness and the critical stain energy release rate are related by

$$G_{Ic} = \frac{1}{E} \, K_{Ic}^2$$

where *E* is the Young's modulus. If an initial crack size is known, then a critical stress can be determined using the strain energy release rate criterion.

Ductile material failure criteria

Criteria used to predict the failure of ductile materials are usually called yield criteria. Commonly used failure criteria for ductile materials are:

- the Tresca or maximum shear stress criterion.
- the von Mises yield criterion or distortional strain energy density criterion.
- the Gurson yield criterion for pressure-dependent metals.
- the Hosford yield criterion for metals.
- the Hill yield criteria.
- various criteria based on the invariants of the Cauchy stress tensor.

The yield surface of a ductile material usually changes as the material experiences increased deformation. Models for the evolution of the yield surface with increasing strain, temperature, and strain rate are used in conjunction with the above failure criteria for isotropic hardening, kinematic hardening, and viscoplasticity. Some such models are:

- the Johnson-Cook model
- the Steinberg-Guinan model
- the Zerilli-Armstrong model
- the Mechanical threshold stress model
- the Preston-Tonks-Wallace model

There is another important aspect to ductile materials - the prediction of the ultimate failure strength of a ductile material. Several models for predicting the ultimate strength have been used by the engineering community with varying levels of success. For metals, such failure criteria are usually expressed in terms of a combination of porosity and strain to failure or in terms of a damage parameter.